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TITLE STUDIES OF COMPLEXES DERIVED FROM 5-ACETYLAMINO-1,2-BENZOQUINONE 2-OXIME AND RELATED LIGANDS

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STUDIES OF COMPLEXES DERIVED FROM 5-ACETYLAMINO-1,2-BENZOQUINONE 2-OXIME AND RELATED LIGANDS

A thesis submitted to the Council for National Academic Awards in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

by

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The Polytechnic of
North London
in colaboration with
SmithKline Beecham Pharmaceuticals

October 1991

Dedicated to my parents

and my brothers

Declaration

Whilst registered as a candidate for this degree the author has not been registered as a candidate for any other award.

H. Barjesteh

Hengameh Barjesteh

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ABSTRACT

5-Acetylamino-1,2-benzoquinone 2-oxime [5-AcqoH] results from the direct nitrosation of 3-acetylaminophenol together with its isomer 3-acetylamino-1,4-benzoquinone 4-oxime [3-AcqoH]. The quinone oximic structure of the former has been indicated by i.r. and n.m.r. studies. In the case of 3-AcqoH this type of structure has been established by X-ray crystallography.

Following a brief review of quinone oximic complexes, a study of the synthesis, properties and structure of Cu(II), Ni(II), Co(III), and Mn(III) complexes of 5-AcqoH is presented. The complexes $Ni(5\text{-}Acqo)_2.nH_2O$ (n = 2-6), $Cu(5\text{-}Acqo)_2$, $Co(5\text{-}Acqo)_3$, and $Mn(5\text{-}Acqo)_2.H_2O$ were prepared by the direct reaction of 5-AcqoH with the appropriate metal(II) chloride or by the nitrosation of 3-acetylaminophenol in the presence of the metal salt. $Co(5\text{-}Acqo)_3$ was also prepared by the reaction of the ligand with $Na_3[Co(NO_2)_6]$. The complex $Na[Co(5\text{-}Acqo)_2(NO_2)_2]$, resulted from the nitrosation of $Na_3[Co(NO_2)_6]$ in the presence of 3-acetylaminophenol. Pyrolysis of $Ni(5\text{-}Acqo)_2.6H_2O$ gave $Ni(5\text{-}Acqo)_2$. The complexes $Cu(5\text{-}Acqo)_2$ and $Ni(5\text{-}Acqo)_2.nH_2O$ (n = 0, 2-6) reacted with pyridine and 2,2'-dipyridyl to give adducts whereas the complexes of $M(5\text{-}Acqo)_3$ (M = Co, Mn) showed no reaction with pyridine.

Magnetochemical measurements, indicated that all complexes, [except $Ni(5\text{-}Acqo)_2$], are magnetically dilute and hence monomeric. $Ni(5\text{-}Acqo)_2$ complex has a subnormal magnetic moment due to association. The diamagnetism of $Co(5\text{-}Acqo)_3$ and the low spin configuration of $Mn(5\text{-}Acqo)_3.H_2O$ are indicative of the strong field character of the ligand. COSY, ^1H- and ^{13}C n.m.r. studies have shown that $Co(5\text{-}Acqo)_3$ is a mixture of *facial* and *meridial* isomers. For all complexes i.r. studies indicate the involvement of the ring CO in bonding. Their electronic spectra show strong absorption in the u.v. region which tails into the visible but d – d transitions have been clearly identified for $Ni(5\text{-}Acqo)_2.6H_2O$ and $Mn(5\text{-}Acqo)_3.H_2O$.

Reexamination of the reaction of several complexes of type $M(Rqo)_2$ [M = Ni or Cu] with dimethyl acetylenedicarboxylate has confirmed the occurence of cycloaddition and the formation of oxazine. A metal-containing product, M(II)(butynedioate), and in some cases an additional organic product, 1,4-benoxazin-2-one, have been isolated. Mechanistic appraisals for the 1,4-benoxazinone formation are presented and the structure of one has been elucidated by X-ray crystallography.

The reaction of the new complex $Cu(5\text{-}Acqo)_2$ with DMAD leads to analogous products. The reaction of the complexes $M(1\text{-}nqo)_2$ [M = Cu, Ni] with methyl propiolate give the hydrated M(II)$(propynoate)_2$ and oxazine.

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Abbreviations

Fig.	figure
i.r.	infra-red
m.s.	mass spectrum
n.m.r.	nuclear magnetic resonance
u.v./vis.	ultra violate/visible
m.p.	melting point
t.l.c.	thin layer chromatography
Ref.	reference(s)
h	hour(s)
chel	chelate
AmONO	amyl nitrite
EtOH	ethanol
EtAc	ethyl acetate
$hfac^-$	hexafluoroacetylacetonato anion
hfacH	hexafluoroacetylacetone
py	pyridine
dipy	2,2'-dipyridyl
3-AcqoH	3-acetylamino-1,4-benzoquinone 4-oxime
5-AcqoH	5-acetylamino-1,2-benzoquinone 2-oxime
5-Acqo^-	5-acetylamino-1,2-benzoquinone 2-oximato anion
1-nqoH	1,2-naphthoquinone 1-oxime
1-nqo^-	1,2-naphthoquinone 1-oximato anion
2-nqoH	1,2-naphthoquinone 2-oxime
2-nqo^-	1,2-naphthoquinone 2-oximato anion

nqoH	1-nqoH or 2-nqoH
qoH	1,2-benzoquinone 2-oxime
qo^-	1,2-benzoquinone 2-oximato anion
DMAD	dimethyl acetylenedicarboxylate
MP	methyl propiolate
EGDE	ethylene glycol dimethyl ether
bd^-	butynedioate anion
pna^-	propynoate anion

CONTENTS

CHAPTER ONE

Synthesis of 5-Acetylamino-1,2-benzoquinone 2-oxime and the Single Crystal X-Ray Structure of 3-Acetylamino-1,2-benzoquinone 4-oxime

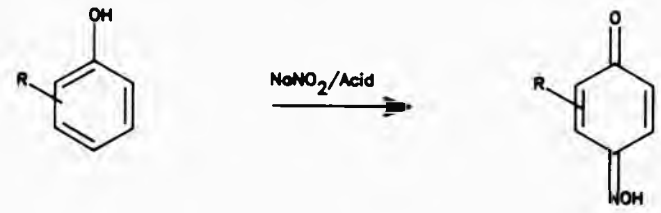
1.1 Preparation of Quinone Mono-Oximes

A variety of direct and indirect methods for the synthesis of 1,2-quinone mono-oximes/2-nitrosophenols have been reported. In the direct methods the 1,2-quinone mono-oxime itself is obtainable from the reaction together with its 1,4-isomer.[1-6] In the case of the indirect methods a metal complex of the 1,2-quinone mono-oxime is first formed from which the free oxime may be isolated.[7-15] The isolation of the free oxime is achievable by acidification of the complex[13] or by passing a solution of the complex over an ion exchange resin.[15] In the case of selected Lewis base adducts of copper(II) 1,2-quinone mono-oximato complexes the isolation of the free oxime has also been achieved by treating their methanolic solutions with silica.[11]

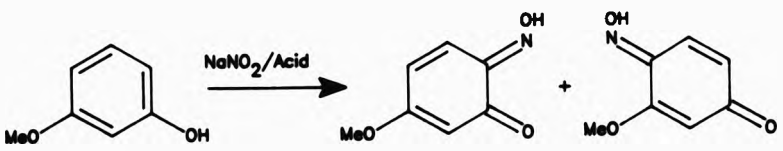
1.1.1 Direct Methods

The principal method employed for the preparation of quinone mono-oximes involves the nitrosation of a phenol with sodium nitrite and dilute aqueous acid. Nitrosation of aromatic compounds is difficult unless activating groups are attached to the aromatic ring, e.g. hydroxy.

The hydroxy group is ortho/para directing and theoretically nitrosation of phenols can yield a mixture of 2- and 4-isomers. In practice for most phenols the predominant product of nitrosation with sodium nitrite/acid is the 4-isomer (Reaction 1.1) and the 2-isomer is only formed in a few cases, e.g. 3-methoxy phenol (Reaction 1.2).[1-3]



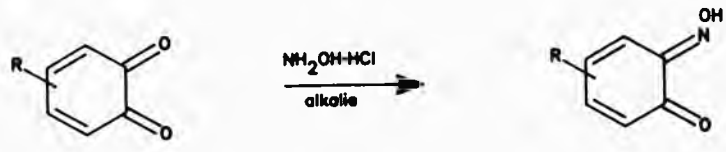
Reaction 1.1



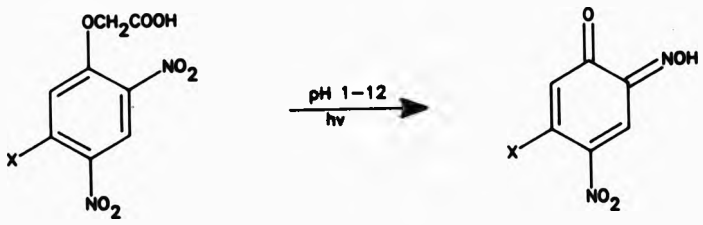
Reaction 1.2

Other direct methods which have been used for the preparation of quinone mono-oximes include the reaction of hydroxylamine hydrochloride with a quinone[4] (Reaction 1.3) and photochemical syntheses. Both these methods have very limited applications. In the case of photochemical synthesis only two reports have appeared

to date. These reports involve the photolysis of 2-nitrophenoxyacetic acids[5] (Reaction 1.4) and that of 1-naphthol in the presence of N-nitrosodimethylamine (Reaction 1.5).[6]

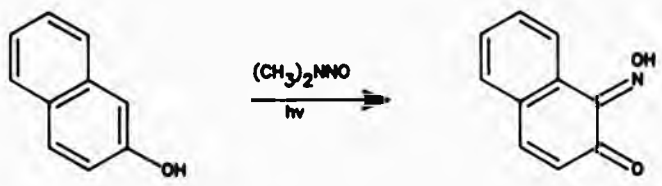


Reaction 1.3



X = H or RO

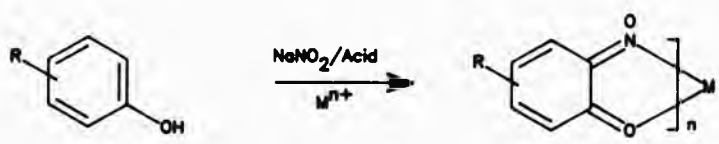
Reaction 1.4



Reaction 1.5

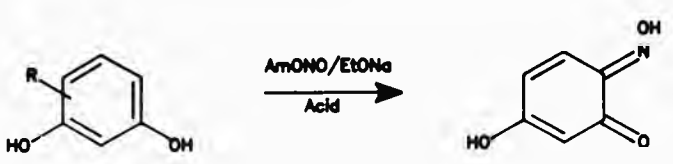
1.1.2 Indirect Methods

Nitrosation of a phenol in the 2-position occurs readily in the presence of a transition metal salt (Reaction 1.6).[7-9] In this case the 1,2-quinone mono oxime is obtained in the form of its metal complex. Significantly, using this approach nitrosation in the 2-position has been accomplished even in the case of phenols which do not afford the 2-nitrosated product on treatment with sodium nitrite/acid.



Reaction 1.6

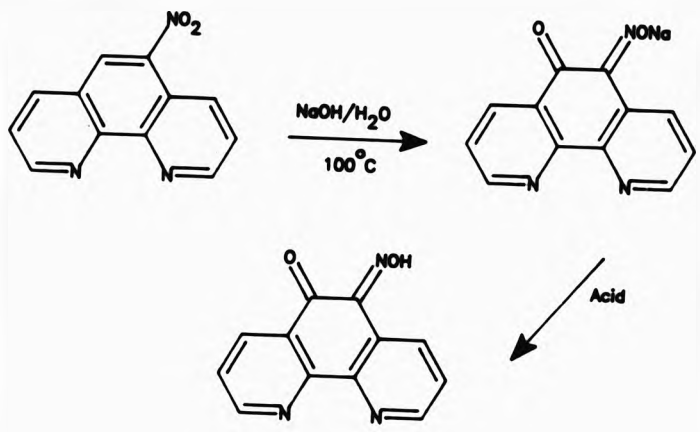
Nitrosation of 3-hydroxyphenols using amyl nitrite and sodium alkoxide leads to similar products (Reaction 1.7).[10] This method has mainly been used for the preparation of 5-hydroxy-1,2-benzoquinone mono-oximes by acidification of their alkali metal complexes.



Reaction 1.7

Recent studies have shown that potassium or sodium complexes of 1,2-naphthoquinone 1-oxime (1-nqoH) and 1,2-naphthoquinone 2-oxime (2-nqoH) can be obtained by reacting their complexes, $M(1\text{-nqo})_2$, $M(2\text{-nqo})_2$ ($M = Cu^{2+}$ or Ni^{2+}), $Cu(2\text{-nqo})_2(dipy)$ or $Cu(2\text{-nqo})(Ph_3P)_2$ with potassium or sodium cyanide.[11] This route to potassium and sodium complexes has a potentially wide range of applicability.

The quinone mono-oxime of 1,10-phenanthroline has been prepared by the acidification of its sodium complex which is obtainable by the alkali induced rearrangement of 5-nitro-1,10-phenanthroline (Reaction 1.8).[12]



Reaction 1.8

The preparation of 1,2-quinone mono-oximes by the acidification of their transition metal complexes has also been reported by several workers.[7,13,14] Generally these reports lack experimental details. In this procedure the metal complex is treated with an aqueous acid and the resultant oxime is extracted with an organic solvent. Solutions of several 1,2-quinone mono-oximes have been prepared but isolation of the oxime from the solution has only been accomplished in very few cases.[13]

Recently, the isolation of 1,2-quinone mono-oximes from their transition metal complexes has successfully been achieved by the use of ion exchange resins. The technique has proved applicable to the preparation of 5-acetylamino-1,2-benzoquinone 2-oxime (5-AcqoH) from

its nickel complex.[15]

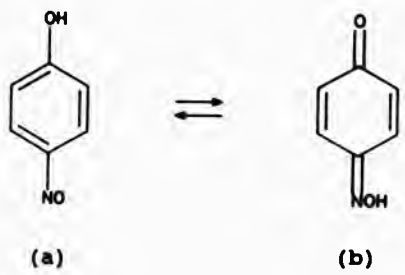
A limited number of 1,2-quinone mono-oximes has been prepared by stirring methanolic solutions of bis(1,2-quinone mono-oximato)copper(II) adducts of 1,10-phenanthroline or 2,2'-dipyridyl with silica. The liberated ligand is isolated by removing the methanol from the reaction mixture and extracting the residue with an organic solvent (Reaction 1.9).[11]

$$Cu(qo)_2 \cdot X \xrightarrow[\text{Methanol}]{\text{Silica}} Cu(qo) \cdot X' + qoH$$

Reaction 1.9

1.2 Structure of Quinone Mono-oximes

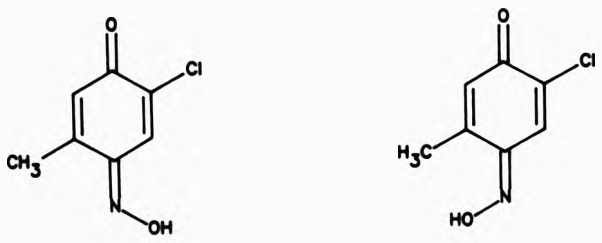
As noted earlier reaction of phenol with $NaNO_2$/acid involves mainly attack on the 4-position and leads to a product which has been isolated in two forms.[16] One of these forms has been assigned a nitrosophenolic structure (Fig. 1.1a) and the other a quinone oximic structure (Fig. 1.1b). A tautomeric equilibrium between these two forms has been suggested to exist in solution. Two forms, yellow crystals and white fibres, have also been isolated in the case of the 4-nitrosated product derived from the nitrosation of



(a) (b)

Fig. 1.1

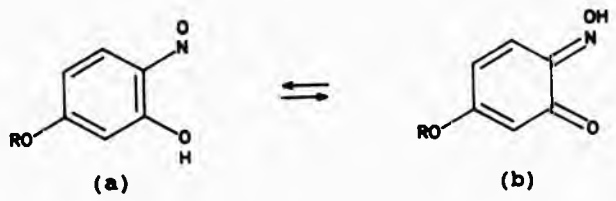
2-chloro-5-methyl-phenol.[17,18] An X-ray crystallographic study of the yellow crystals has revealed it has quinone oximic structure with the OH of the NOH group *syn* to the chlorine (Fig. 1.2a).[17] From chemical evidence and the knowledge of the structure of the *syn* form, an *anti* quinone oximic structure (Fig. 1.2b) has been suggested for the white fibres.[18] Similar proposals have been made for the product of nitrosation of 2-bromo-5-methylphenol which has also been isolated in a yellow crystalline form and as white fibres.[18]



(a) (b)

Fig. 1.2

The 2-nitrosated products arising from the nitrosation of some phenols with $NaNO_2$/acid have also been isolated in two forms. For example, the product arising from the nitrosation of 3-methoxyphenol in the 2-position (Fig. 1.3, R = Me) was found to crystallise as green rectangular plates from benzene and as red needles from ethanol.[19] Initially, the quinone oximic structure (Fig. 1.3b) was assigned to the red form (α-form) and the nitrosophenolic structure (Fig. 1.3a) to the green form (β-form). An X-ray crystallographic study of the α-form showed it to have quinone oximic structure with the OH of the NOH group *anti* to the CO group (Fig. 1.4a).[20] In the case of the 5-propoxy-1,2-benzoquinone 2-oxime which also exists in



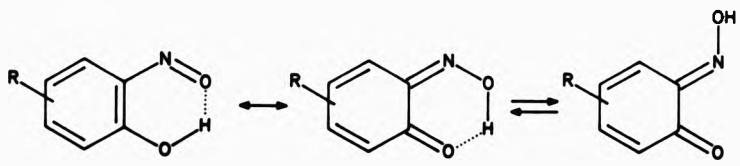
(a) (b)

Fig 1.3

(a) (b)

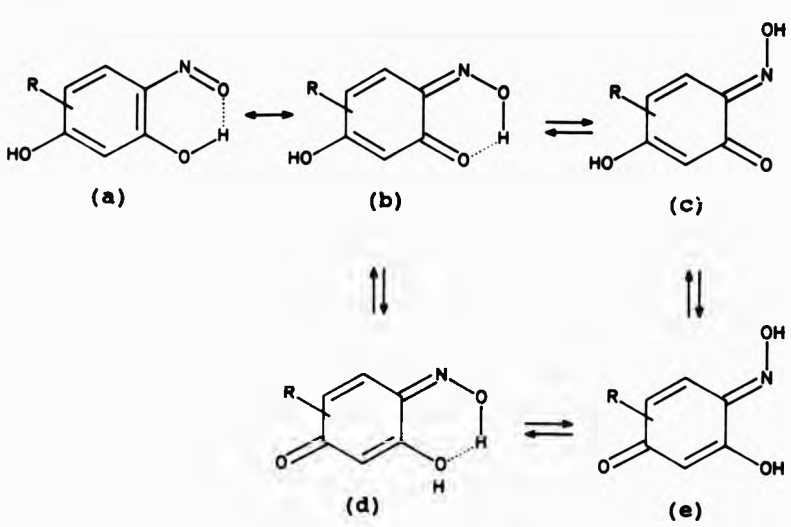
Fig. 1.4

α- and β-forms, X-ray studies showed the latter to be quinone oximic rather than nitrosophenolic.[21] However, in this case the compound has the OH of the NOH group *syn* to the CO group (Fig 1.4b). The significance of the oximic structure has also been demonstrated by the finding that the related 4-nitrosated product, 3-hydroxy-2-methyl-1,4-benzoquinone 4-oxime which has been characterised by X-ray crystallography has a quinone oximic structure in the solid state.[22] In solution, i.r., u.v. and n.m.r. studies have indicated the presence of an equilibrium between quinone oximic and nitrosophenolic species for both 2- and 4-nitrosated compounds.[23-27] In view of the above the 1,2-quinone mono-oxime/2-nitrosophenol system may be represented as shown in Scheme 1.1. Because of the important contribution from the oximic forms, in this thesis the compounds have been referred to as quinone mono-oximes.



Scheme 1.1

In the case of 5-hydroxy-1,2-benzoquinone mono-oximes additional contribution from the 1,4-quinone 4-oxime isomers is also a possibility (Scheme 1.2). As mentioned

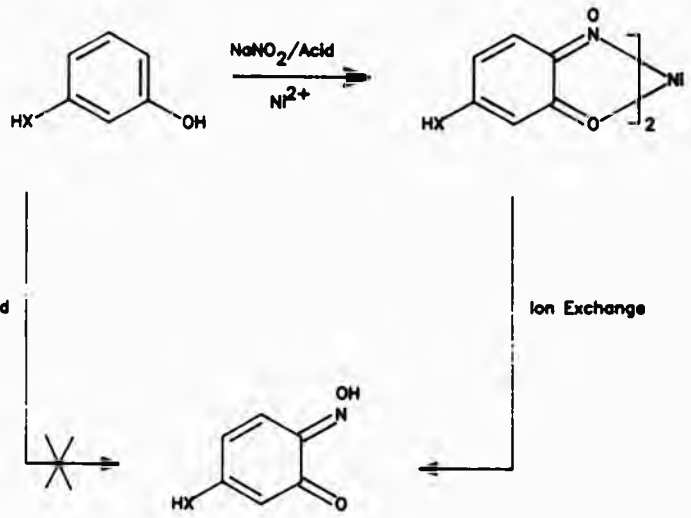


Scheme 1.2

earlier X-ray crystallographic studies have shown that the product arising from the nitrosation of 3-hydroxy-2-methylphenol exists in the 1,4-quinone 4-oxime form (e in Scheme 1.2) rather than in an 1,2-quinone 2-oxime form.[22]

1.3 Synthesis of 5-Acetylamino-1,2-benzoquinone 2-oxime

Previously 5-acetylamino-1,2-benzoquinone 2-oxime was obtained by ion exchange of its nickel complex (Scheme 1.3).[15] It has also been reported that the direct nitrosation of 3-acetylaminophenol leads to a mixture of products which shows no tendency to form complexes with various metal ions (e.g. iron).[15]



X = $NCOCH_3$

Scheme 1.3

During this study and contrary to previous reports it has been found that the nitrosation of 3-acetylaminophenol at room temperature gives an orange solid which readily reacts with iron(II) salts to give intensely coloured green products. This suggests the formation of a complexing ligand. T.l.c. examination of the crude product showed the presence of three components which were separated by column chromatography. Elution with toluene gave firstly a yellow product which is either 3-acetylamino-4-nitrophenol or 5-acetylamino-2-nitrophenol. The second yellow component eluted with toluene:ethyl acetate, was characterised as 3-acetylamino-1,4-benzoquinone 4-oxime.

The major product, 5-acetylamino-1,2-benzoquinone 2-oxime was also eluted with toluene:ethyl acetate. Significantly it was also observed that nitrosation of the phenol at low temperatures (*ca.* -10 °C) improves the yield of the latter considerably.

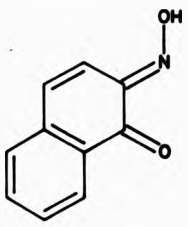
The formation of the nitrophenol is not surprising as nitrous acid, generated in *situ*, could oxidise the initially formed nitroso compound to the nitro product.[28] The formation of 3-acetylamino-1,4-benzoquinone 4-oxime has also been observed when the phenol is nitrosated in presence of transition metal salts.

5-Acetylamino-1,2-benzoquinone 2-oxime chelates transition and main group metal salts to give the corresponding metal complexes (see Chapter 2). In contrast 3-acetylamino-1,4-benzoquinone 4-oxime shows no reaction with transition metal salts and only limited reaction with main group metal compounds (e.g. sodium hydroxide).

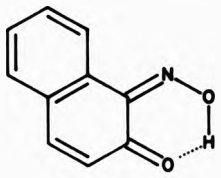
1.4 Structure of 5-Acetylamino-1,2-benzoquinone 2-oxime

Some information regarding the structure of 5-acetylamino-1,2-benzoquinone 2-oxime has been obtained by studying its i.r. and ^{1}H n.m.r. spectra.

Previously, on the basis of i.r. studies an *anti* structure has been suggested for 1,2-naphthoquinone 2-oxime (Fig. 1.5a) and a *syn* structure for 1,2-naphthoquinone 1-oxime (Fig. 1.5b).[25] Subsequently, the proposed structure for the latter was confirmed by X-ray crystallographic studies.[29] In the case of 1,2-naphthoquinone 2-oxime the absorption due to νCO is observed at 1668 cm^{-1} where as in the 1-isomer the corresponding absorption occurs at 1618 cm^{-1}. This difference reflects the absence of intramolecular hydrogen bonding in the former.



(a)



(b)

Fig. 1.5

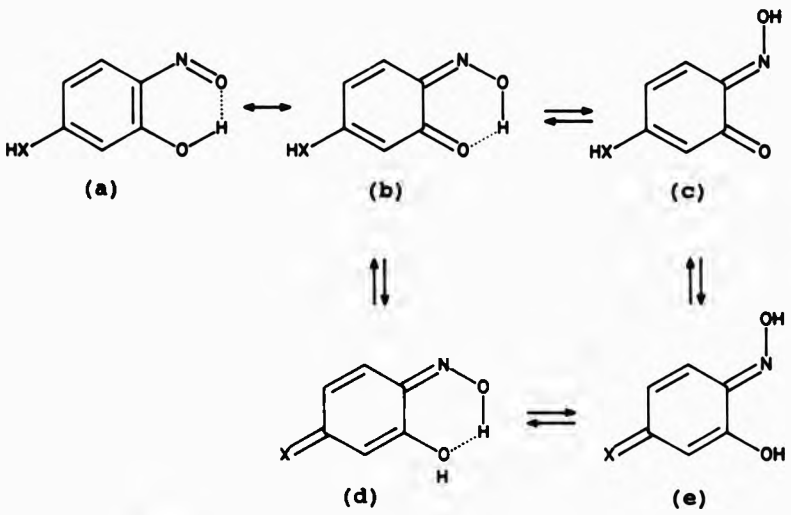
In metal chelates derived from 1,2-naphthoquinone 1-oxime the absorption due to νCO shifts slightly (*ca.* 10 cm^{-1}) to lower frequency relative to the νCO of the protonated ligand (Table 2.1). In contrast in metal chelates derived from 1,2-naphthoquinone 2-oxime the corresponding shift is more pronounced (*ca.* 40 cm^{-1}) (Table 2.1).

Table 2.1 νCO Band Assignments for 1,2-Quinone Mono-oximes and some of their Metal Complexes

Compound	νCO (cm^{-1})	References
1-nqoH	1618	25
$Cu(1\text{-nqo})_2$	1610	30
$Mn(1\text{-nqo})_2$	1610	31
$Mn(1\text{-nqo})_3$	1605	31
$Fe(1\text{-nqo})_3$	1610	30, 32
$Cr(1\text{-nqo})_3$	1608	31
Li(1-nqo)	1620	33
Li(1-nqo)(1-nqoH)	1665, 1618	33
Li(1-nqo)(1-nqoH).EtOH	1660, 1620	33
2-nqoH	1668	25
$Cu(2\text{-nqo})_2$	1618	30
$Mn(2\text{-nqo})_2$	1615	31
$Mn(2\text{-nqo})_3$	1625	31
$Fe(2\text{-nqo})_3$	1620	30
$Cr(2\text{-nqo})_3$	1620	30
Li(2-nqo)	1620	33
Li(2-nqo).1/2EtOH	1618	33
Li(2-nqo)(2-nqoH)	1670, 1618	33
Li(2-nqo)(2-nqoH).EtOH	1668, 1620	33
5-AcqoH	1642	15, •
$Cu(5\text{-Acqo})_2$	1601	•
$Ni(5\text{-Acqo})_2$	1601	•
$Ni(5\text{-Acqo})_2.6H_2O$	1639	•
$Fe(5\text{-Acqo})_3$	1600	15
$Mn(5\text{-Acqo})_3.H_2O$	1591	•
$Co(5\text{-Acqo})_3$	1598	•
$Na[Co(5\text{-Acqo})_2(NO_2)_2]$	1598	•
$[Co_2(5\text{-Acqo})_5]O_2$	1598	•

•=This work

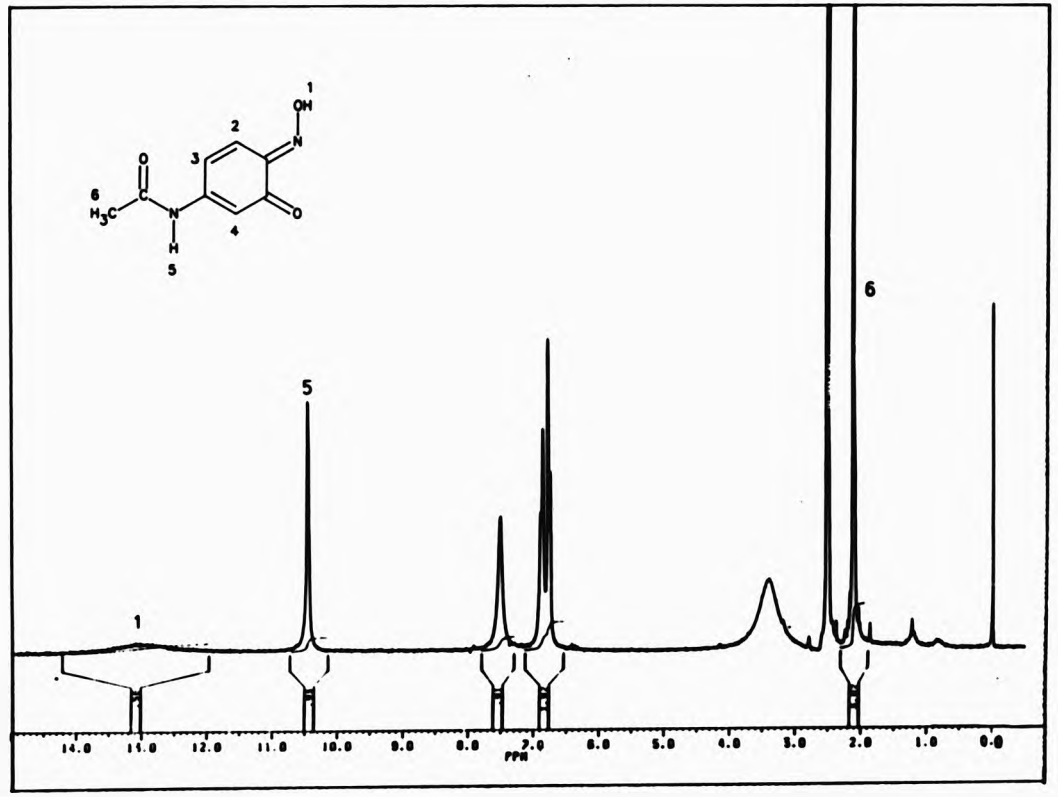
In the case of of 5-acetylamino-1,2-benzoquinone 2-oxime two νCO bands are observed at 1694 cm^{-1} and 1642 cm^{-1} assignable to the amide and the quinone oximic carbonyl groups respectively. On complexation the quinone oximic carbonyl group shifts to *ca.* 1600 cm^{-1}. By analogy to the above, an *anti* oximic structure (c in Scheme 1.4) is suggested for 5-acetylamino-1,2-benzoquinone 2-oxime in the solid state.



Scheme 1.4

The ^1H n.m.r. spectrum of 5-acetylamino-1,2-benzoquinone 2-oxime in d_6-dimethylsulphoxide (d_6-DMSO) (Fig. 1.6a) shows the presence of two acidic hydrogens at 13.1 and 10.5 ppm. The former is assignable to the oximic hydrogen (NOH) by analogy to other related oximic

Fig. 1.6a ^{1}H n.m.r. Nuclear Magnetic Resonance Spectrum of 5-Acetylamino-1,2-benzoquinone 2-oxime in d_6-DMSO



compounds such as 5-hydroxy-6-methyl-1,2-benzoquinone 2-oxime[15] and 1,4-naphthoquinone 4-oxime.[34] Significantly, the ^{1}H n.m.r. spectrum (Fig. 1.7) of 3-acetylamino-1,4-benzoquinone 4-oxime also shows an acidic hydrogen at 13.6 ppm. The latter has been proven to exist in the quinone oximic form by X-ray chrystallography (see Section 1.7). In contrast, in the ^{1}H n.m.r. spectrum of the acetylated nitrophenol (Fig. 1.8) the acidic hydrogens are observed in the range 10-11 ppm, thus indicating the absence of an oximic hydrogen. The ^{1}H n.m.r. spectrum of 5-acetylamino-1,2-benzoquinone 2-oxime also shows the expected resonances due to the methyl and aromatic hydrogens. However, resonances due to the aromatic protons become better resolved after the addition of deuterium oxide (D_2O) (Fig. 1.6b).

Fig. 1.7 ^{1}H n.m.r. Nuclear Magnetic Resonance Spectrum of 3-Acetylamino-1,4-benzoquinone 4-oxime in d_6-DMSO

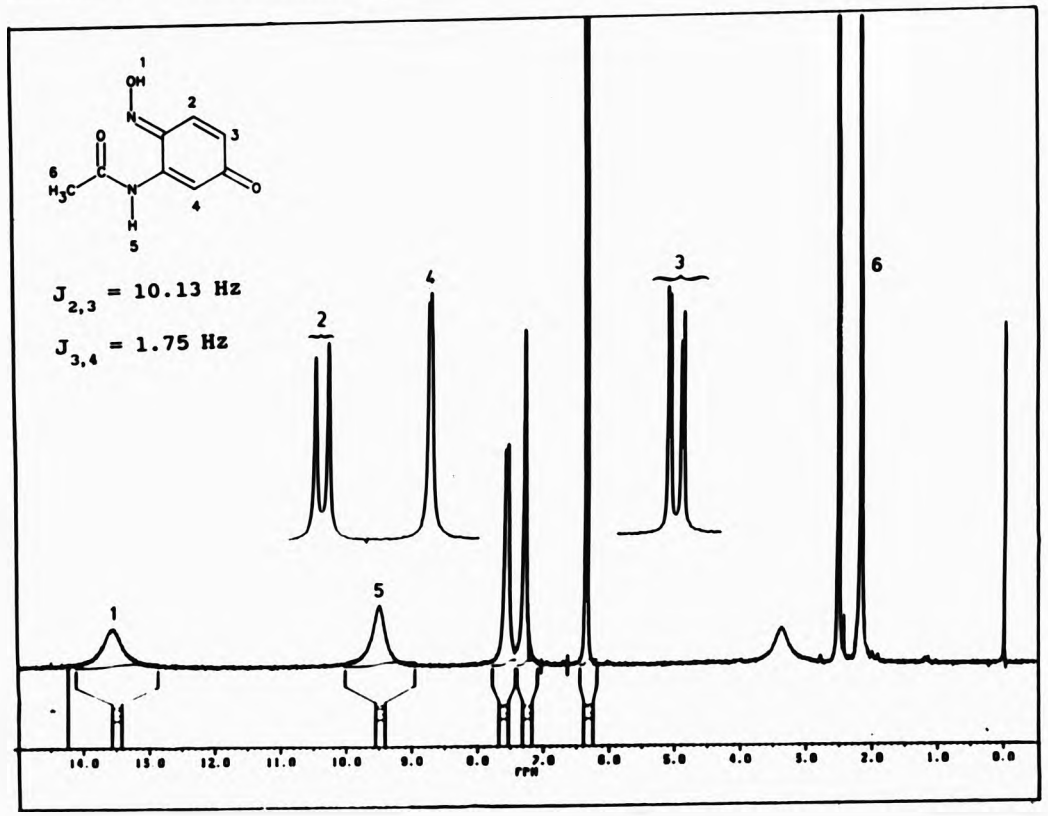


Fig. 1.8 ^{1}H n.m.r. Nuclear Magnetic Resonance Spectrum of 3-Acetylamino Nitrophenol* in d_6-DMSO

*Although 3-Aceylamino-4-nitrophenol is shown the n.m.r. results are also compatible for 5-acetyamio-2-nitrophnol

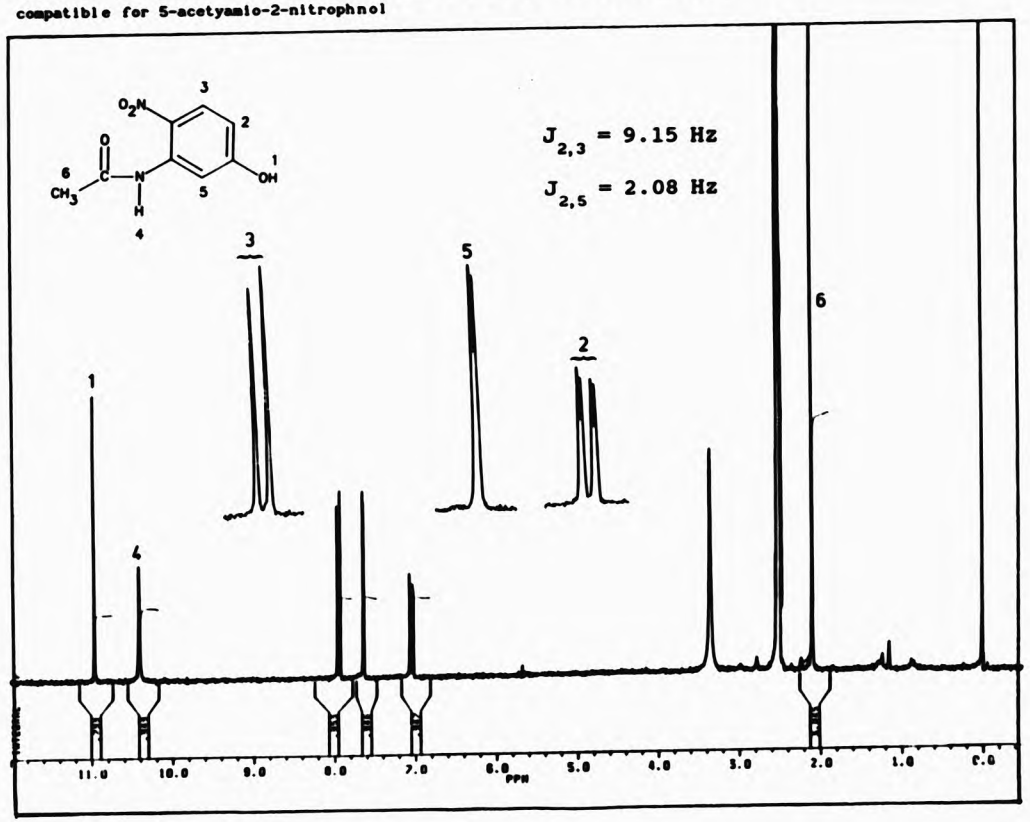
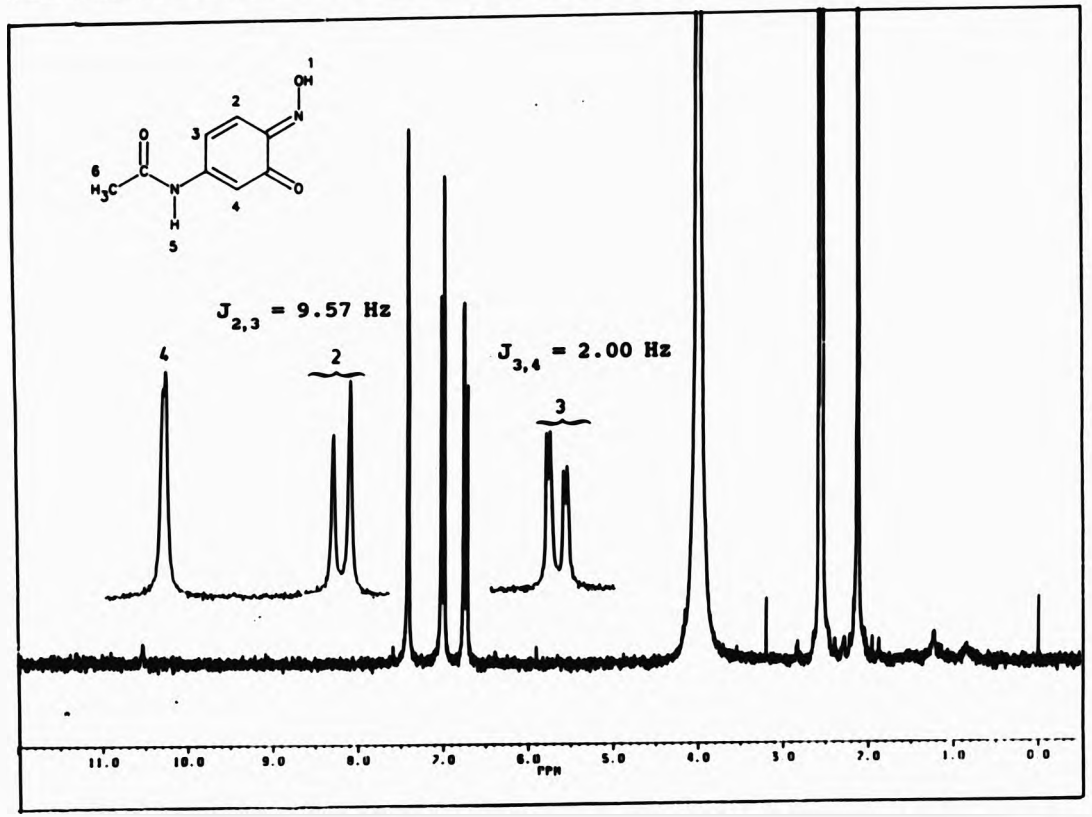
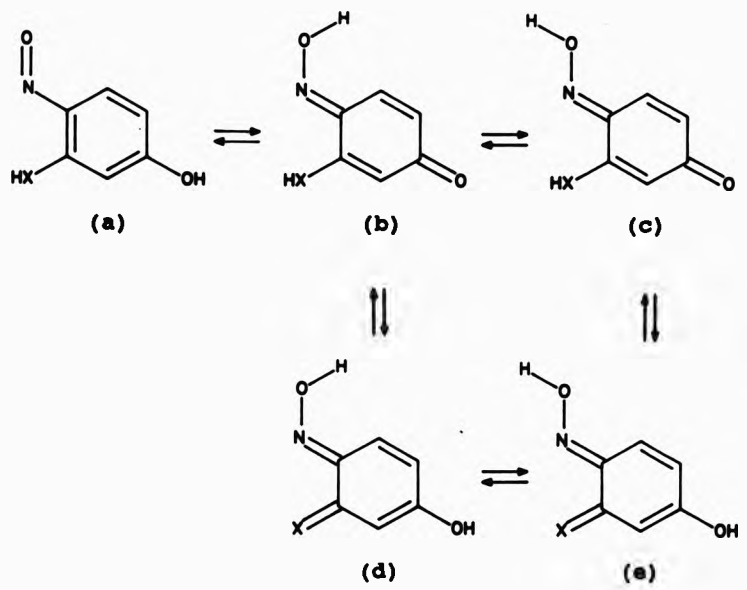


Fig. 1.6b ^1H n.m.r. Nuclear Magnetic Resonance Spectrum of 5-Acetylamino-1,2-benzoquinone 2-oxime after the addition of D_2O



1.5 The Single Crystal X-Ray Structure of 3-Acetylamino-1,4-benzoquinone 4-oxime

As discussed earlier quinone mono-oximes can have various structures and in solution may exhibit nitrosophenolic/quinone oximic tautomerism.[23-27] Similarly, 3-acetylamino-1,4-benzoquinone 4-oxime can exhibit a number of isomeric and tautomeric structures (Scheme 1.5).



Scheme 1.5

The structure of several 1,2- and 1,4-quinone mono-oximes have been determined by X-ray crystallography.[17,20,22,35-38] These studies have shown that the ligand is essentially quinone oximic in character. This is indicated by the presence of four long and two short C – C ring bond lengths, and relatively short C – O and C – N bond lengths (Table 1.2). During the present study an X-ray crystallographic structure determination of 3-acetylamino-1,4-benzoquinone 4-oxime has shown that in the solid state this compound has the 1,4-quinone oximic structure (b in Scheme 1.5).

1.5.1 Crystal Data for 3-Acetylamino-1,4-benzoquinone 4-oxime

$C_8H_7N_2O_3$, M = 179.15, a = 16.65(3), b = 12.75(3), c = 3.84(1), $\alpha = \gamma = 90.00^\circ(2)$, $\beta = 94.39^\circ(2)$, U = 813 $Å^3$. F(000) = 320.00, μ(Mo-K_α) = 10.00 cm^{-1}, Z = 4, D_c = 1.26 gcm^{-3}.

1.5.2 Crystal Preparation and Data Collection

3-Acetylamino-1,4-benzoquinone 4-oxime was synthesized by nitrosation of 3-acetylaminophenol in presence of a transition metal salt (see Chapter 2) and was recrystallised from ethyl acetate. The crystal selected for the X-ray study had dimensions

Table 1.2 Bond Lengths of 1.2-Quinone Mono-oximes from Previous X-Ray Studies

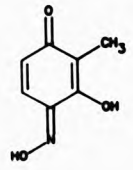
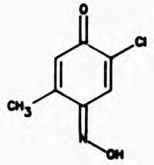
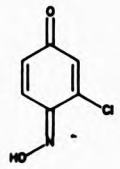
Quinone mono-oxime		Bond length (Å)					Ref.
Structure	No.	C-O	C-N	N-O	C-C†	C-C‡	
	(I)	1.25	1.28	1.36	1.33	1.45	22
	(II)	1.21	1.28	1.32	1.31	1.47	17
	(III)	1.20	1.25	1.39	1.33	1.46	35

Table 1.2 cont.

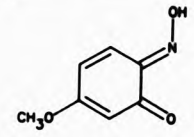
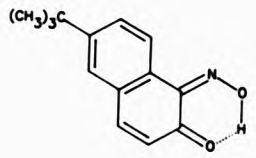
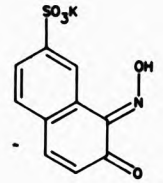
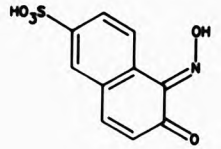
Quinone Mono-oxime		Bond Length (Å)					Ref.
Structure	No.	C-O	C-N	N-O	C-C†	C-C‡	
	(IV)	1.23	1.22	1.36	1.34	1.46	20
	(V)	1.24	1.30	1.36	1.37	1.47	36
	(VI)	1.22	1.31	1.39	1.31	1.47	37

Table 1.2 cont.

Quinone mono-oxime		Bond length (Å)					Ref.
Structure	No.	C-O	C-N	N-O	C-C†	C-C‡	
	(VII)	1.24	1.30	1.38	1.33	1.46	38

†=Average bond length of the 2 short bonds, ‡=Average bond length of the 4 long bonds

0.30 X 0.16 X 0.12 mm. The data were collected on a Philips PW1100 diffractometer in the range $3^{\circ} \leq \theta \leq 25^{\circ}$, with a scan width of 0.9°.[39] Using a graphite monochromated Mo-K_{α} radiation source, a total of 1382 unique reflections with $I/\sigma(I) > 3$ were collected. The intensity relationship $I_{hkl} = I_{\bar{h}kl} = I_{h\bar{k}l} = I_{\bar{h}\bar{k}l}$ observed for selected strong reflections confirmed the presence of a primitive monoclinic crystal system. The data were corrected for absorption, the Lorentz and polarisation effects.

1.5.3 Structure Solution and Refinement

Systematic absences in the data of the type: 0k0; $k = 2n + 1$ and h0l; $h + l = 2n + 1$ indicated a space group $P2_1/n$. This was confirmed by complete structure solution in this space group. The structure was solved by direct methods using SHELXS-86[40] structure solution programme for obtaining the coordinates of the phenol ring. Subsequent difference Fourier maps revealed the position of remaining non-hydrogen atoms. Also difference Fourier calculations, with $\sin\theta < 0.35$, revealed the position of all the hydrogen atoms. The hydrogen atoms were included in the structure factor with isotropic thermal parameters of 0.06599 $Å^2$. Anisotropic thermal parameters were assigned to the oxygen and nitrogen atoms in the final full-matrix least square refinement, which converged to R = 0.0539

($R = \Sigma[F_o - F_c]/\Sigma[F_o]$), and $R_w = 0.0520$ ($R_w = \Sigma[F_o - F_c]W^{1/2}/\Sigma[F_o]W^{1/2}$), with weights of $1/\sigma^2(F)$ assigned to individual reflections.

All the atomic coordinates, temperature factors, bond lengths, intra bond angles, intra and inter-molecular distances, are given in Tables 1-7 in Appendix 1.

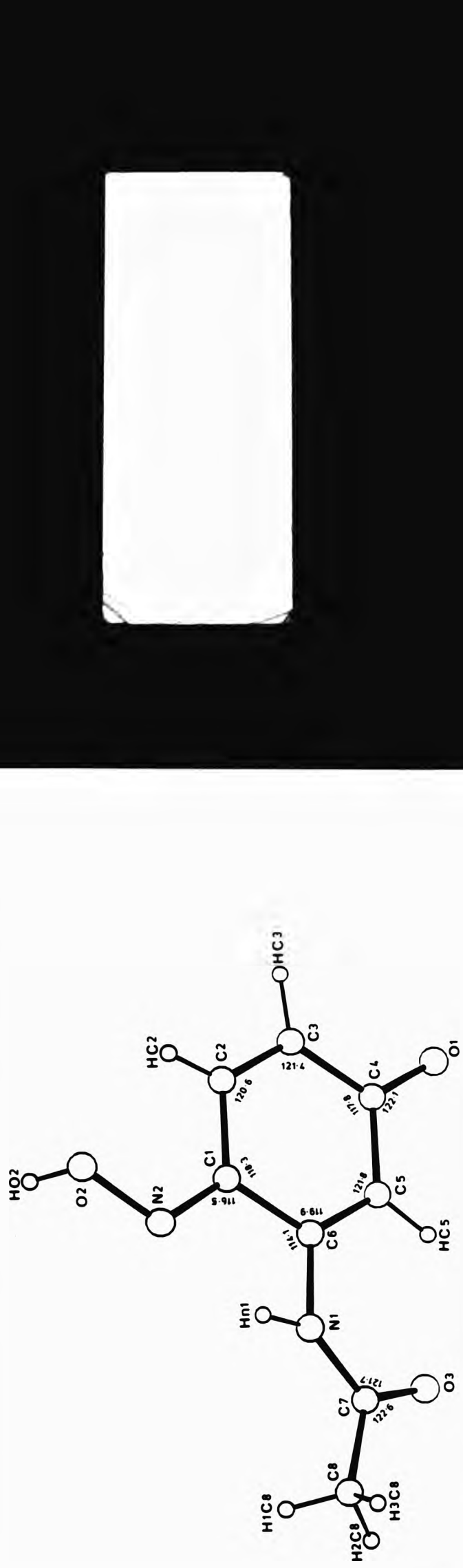
1.5.4 Results and Discussion

Selected bond lengths and bond angles for 3-acetylamino-1,4-benzoquinone 4-oxime are shown in Fig. 1.10 and Fig. 1.11.

Comparison of the bond length of the ring CO group in the structure of 3-acetylamino-1,4-benzoquinone 4-oxime (Fig. 1.10) to those tabulated for compounds with established quinone mono-oxime structures in Table 1.2 shows that the bond C(4) - O(1) [1.232(7) Å] is within the range quoted for compounds (I - VII). The N – O bond length of 1.372(6) Å is also very similar to those reported previously. However,the bond length of N(2) - C(1) [1.301(7) Å], appears in the upper range of C = N bond distances reported for the related structures shown in Table 1.2. Furthermore the C = N and N – O bond distances are similar to those found in oximes, e.g. formamidoxime (C = N, 1.29 Å; N – O, 1.42 Å)[41] whereas the C – O bond is similar to those found in quinones, e.g.

Fig. 1.10 Selected Bond Lengths (Å) in 3-Acetylamino-1,4-benzoquinone 4-oxime

Fig. 1.11 Selected Bond Angles (°) in 3-Acetylamino-1,4-benzoquinone 4-oxime



1,4-benzoquinone (1.22 Å).[42] Significantly in the structure determined the ring C=O has similar bond length to the C=O [1.22(5) Å] of the amide group. Another significant observation arising from this study is that in line with the structure of other 1,4-isomers (see Table 1.2) the OH of the NOH is *anti* to the group closest to it i.e. in this case the acetyl group. The ring C–C bond distances show that two C–C bonds are shorter than the remaining four C–C bonds (Fig. 1.10). The short bonds are the C(2)–C(3) and C(5)–C(6) which are 1,4 with respect to each other. The mean bond length of these bonds (1.339 Å) is 0.101 Å shorter than the mean of the remaining bonds, indicating that they have more double bond character.

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CHAPTER TWO

Studies of Metal Complexes Derived from 5-Acetylamino-1,2-benzoquinone 2-oxime

2.1 Introduction

The aim of this part of the thesis was to investigate the synthesis of copper, nickel, cobalt, and manganese complexes derived from 5-acetylamino-1,2-benzoquinone 2-oxime. This ligand was chosen due to the presence of the acetylamino group (-NHAC) which is expected to be hydrophilic and therefore of some value in the treatment of metal overload diseases. The complexes have been studied by elemental analysis, room temperature magnetic measurements, i.r., u.v./vis. and where possible n.m.r. spectroscopy.

2.2 Metal Complexes of 1,2-Quinone Mono-oximes

Metal complexes of 1,2-quinone mono-oximes have been known for a considerable length of time.[1] The ability of these chelating agents to precipitate certain metal ions has led to their extensive use as analytical and extraction reagents.[2,3] Many such complexes have also found uses in catalysis,[4] the dye industry and in the filtration of tobacco smoke,[5,6] For example iron(II) quinone oximic complexes have shown potential as catalysts for the aerobic oxidation of various types of

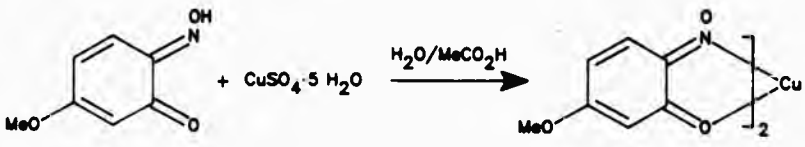
organic compound[7] and 1,2-naphthoquinone mono-oximes have been used in the dyeing of polypropylene fibres.[8]

2.2.1 Preparation of Complexes of 1,2-Quinone Mono-oximes

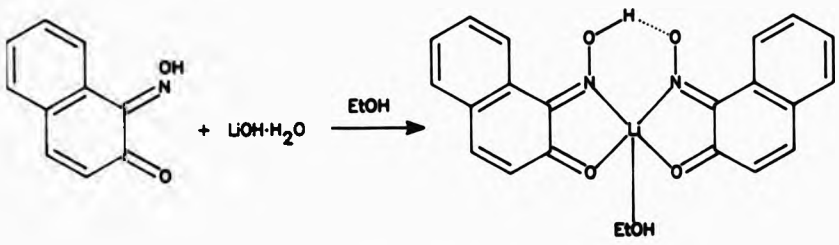
The methods of preparation of the metal complexes of 1,2-quinone mono-oximes may be classified into the following groups, namely:

(a) The direct method.
(b) The nitrosation method.
(c) The interaction of the free ligand with a metal carbonyl.
(d) The Baudish reaction.
(e) The amyl nitrite method.
(f) The nitro rearrangement reaction.
(g) The reaction of transition metal complexes of 1,2-quinone mono-oximes with an alkali metal cyanide.

The *direct method* involves the interaction of a 1,2-quinone mono-oxime with a metal salt[9] or hydroxide.[10] As there are only a few 1,2-quinone mono-oximes available, this method has limited application but can be utilised for the preparation of both main group and transition metal complexes (e.g. Reactions 2.1 and 2.2).

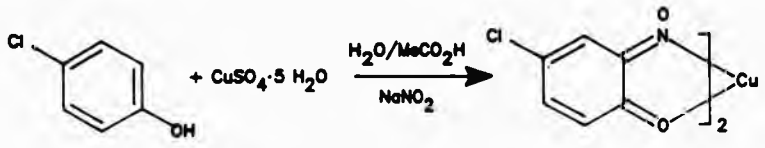


Reaction 2.1



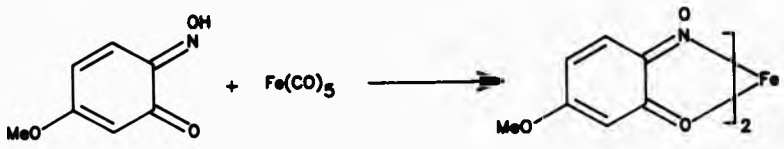
Reaction 2.2

The *nitrosation method* was first reported by Cronheim[11] and later modified in these laboratories. This involves the nitrosation of a phenol, using sodium or potassium nitrite and acetic acid, in the presence of a transition metal salt (e.g. Reaction 2.3). Using this method many complexes of first row transition metals e.g. copper(II),[9] nickel(II),[12,13] iron(III),[14] and cobalt(III),[15] as well as those of some second row transition metals e.g. ruthenium(II)[16] and iridium(III)[17] have been prepared.

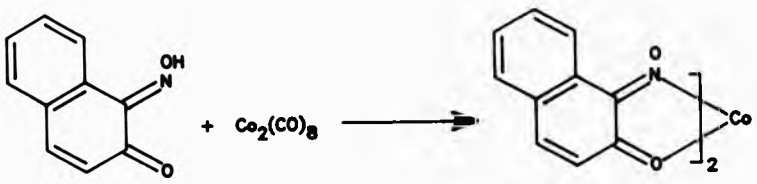


Reaction 2.3

Complexes of some transition metals such as those of iron(II) and cobalt(II) 1,2-quinone mono-oximato complexes have also been prepared by the direct reaction of the free ligand with iron pentacarbonyl or dicobalt octacarbonyl respectively, (e.g. Reactions 2.4 and 2.5).[18,19,20,21]



Reaction 2.4

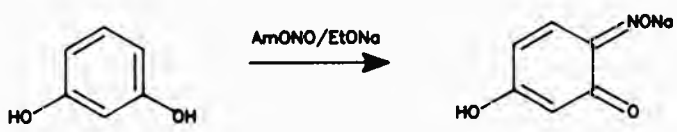


Reaction 2.5

Some copper(II) complexes have been prepared by the *Baudish method*[22] which involves oxidation of an aromatic

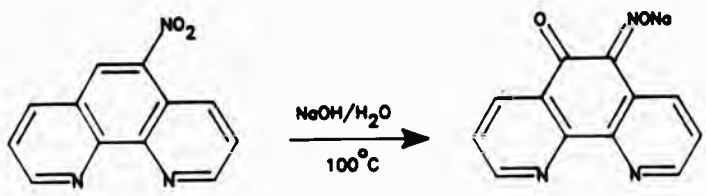
hydrocarbon by the action of hydrogen peroxide and hydroxylamine hydrochloride in the presence of a copper(II) salt. This method, however, must be treated with scepticism as limited preparative and no analytical data were presented in the relevant paper.

The *amyl nitrite method*, has so far been applied for the synthesis of main group metal complexes derived from 5-hydroxy-1,2-benzoquinone 2-oximes. This method involves treatment of a 3-hydroxyphenol with amyl nitrite and an alkali metal hydroxide or alkoxide in ethanol. (e.g. Reaction 2.6).[23,24]



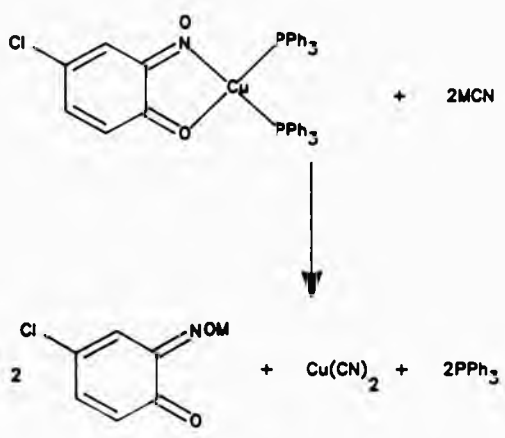
Reaction 2.6

The sodium complex of 1,10-phenanthroline-5,6-quinone 6-oxime has been obtained by the sodium hydroxide induced rearrangement of 5-nitro-1,10-phenanthroline (Reaction 2.7).[25] This method has also been used for the preparation of other sodium quinone mono-oximates derived from heterocyclic nitro compounds.



Reaction 2.7

Recent studies have shown that the reaction of nickel[26] and copper[26,27] complexes of 1,2-quinone mono-oximes or their Lewis base adducts [e.g. $Cu(2\text{-nqo})_2(dipy)$ or $Cu(2\text{-nqo})(Ph_3P)_2$] with an alkali metal cyanide affords the corresponding alkali metal complex. This method has so far been employed for the preparation of the potassium complexes of 4-chloro-1,2-benzoquinone 2-oxime and the sodium and potassium complexes of the mono-oximes of 1,2-naphthoquinone (e.g. Reaction 2.8).



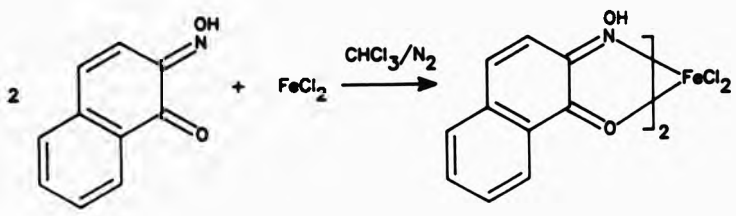
Reaction 2.8

2.2.2 Types of Complexes of 1,2-Quinone Mono-oximes

The complexes derived from 1,2-quinone mono-oximes are of two basic types:

(i) Those involving the anion (qo^-) of a 1,2-quinone mono-oxime, e.g. $Cu(4\text{-}Clqo)_2$, $Ni(4\text{-}Meqo)_2$ and Li(1-nqo).[9,13,10] As indicated in the previous section these complexes are prepared in a variety of ways and are by far the most common.

(ii) Complexes involving neutral 1,2-quinone mono-oximes (qoH) as the ligands, e.g. $(1\text{-}nqoH)_2FeCl_2$ and [Li(1-nqo)(1-nqoH)(EtOH)].[10,28] These are obtainable by the direct reaction of the ligand with a metal hydroxide or halide (e.g. Reactions 2.2 and 2.9). In addition to the above, a complex involving a protonated 1,2-quinone mono-oxime species, $[qoH_2]_2[CuCl_4]$ has been reported to result from the reaction of bis(1,2-benzoquinone 2-oximato)copper(II) with hydrogen chloride gas in ethanol.[9]



Reaction 2.9

2.2.3 The Structure of Complexes of Quinone Mono-oximes

A considerable number of X-ray crystallographic studies of several transition and main group metal complexes of 1,2-quinone mono-oximes have been reported. Some selected data are presented in Table 2.1.

These studies have shown that in all cases the ligands are quinone oximic in character (Fig. 2.1a) rather than nitrosophenolic (Fig. 2.1b).[10,16,17,29-34] This feature is indicated by the presence of two short and four long carbon-carbon bond distances in the ligand. Furthermore it has been observed that the C-O and the C-N bond lengths of the ligand in these complexes are shorter than the C-O bond length in salicylaldoximates[35] (ca. 1.40 °A) and the C-N bond length in 1,8-dinitrosonaphthalene[36] (ca. 1.44 °A). Since the relevant bond lengths in salicylaldoximates and 1,8-dinitrosonaphthalene have essentially single bond character, these observations confirm the predominance of the quinone oximic structure in metal quinone

(a) (b)

Fig. 2.1

Table 2.1 Selected Bond Length of Metal Complexes of 1,2-Quinone Mono-oximes

Complex (qoH)	Bond Length (Å) C – O	C – N	N – O	C – C†	C – C‡	Ref.
$Cu(qo)(H_2O)$ (1,2-naphthoquinone 2-oxime)	1.28	1.35	1.26	1.39	1.44	29
$Cu(qo)_2(Me_2CO)_2$ (1,2-naphthquinone 1-oxime)	1.29	1.35	1.26	1.38	1.44	30
$Cu(qo)(Ph_3P)_2$ (1,2-naphthoquinone 1-oxime)	1.26	1.37	1.29	1.40	1.44	31
$Cu(qo)_2(py)$ (4-methyl-1,2-benzoquinone 2-oxime)	1.27	1.35	1.25	1.35	1.43	32
$K[(Ni(qo)_3](Me_2CO)$ (4-chloro-1,2-benzoquinone 2-oxime)	1.25	1.33	1.27	1.35	1.45	33
$Ru(qo)_2(py)_2$ (1,2-naphthoquinone 1-oxime)	1.28	1.38	1.27	-	-	16
$[UO_2(qo)_2(H_2O)_2].1/2CH_3Cl$ (1,2-naphthquinone 2-oxime)	1.23	1.30	1.34	1.32	1.45	34
$UO(qo)_2(Ph_3PO)(H_2O)$ (1,2-naphthoquinone 1-oxime)	1.25	1.33	1.35	1.37	1.46	34
Li(qo)(qoH)(EtOH) (1,2-naphthoquinone 1-oxime)	1.25	1.31	1.36	1.33	1.48	10

†=Average bond length of 2 short C-C bonds; ‡=Average bond length of 4 long bonds

mono-oximates. The X-ray crystallographic studies also indicate that apart from few exceptions, the ligand to metal mode of bonding involves chelation via the nitrogen atom of the NO group and the quinone oxygen (Fig. 2.1).[10,16,17,29-33]

The possibility of ligand coordination to the metal via the oxygen atom of the NO group and the quinone oxygen has also been suggested but no such example has so far been established crystallographically.[37,38] Another type of ligand attachment, involving bonding only through the nitrogen and the oxygen atoms of the NO group, has been reported in the case of the dioxouranium(VI) complexes $UO_2(1\text{-nqo})_2(Ph_3PO)(H_2O)$ (Fig. 2.2) and $UO_2(2\text{-nqo})_2(H_2O)_2.1/2CHCl_3$.[34] Bonding involving the NO group has also been observed in platinum complexes derived from the related ligand 4-isonitroso-3(R)-isoxazol-5-one.[39] However in these complexes, the bonding to the metal is only through the nitrogen atom of the NO group (Fig. 2.3). Another type of bonding of the ligand to the metal has been observed in the potassium complex of 4-chloro-1,2-benzoquinone 2-oxime, $K(Clqo).{}^1/_2\ H_2O$ (Fig 2.4).[40] In this case , the X-ray crystallographic studies have shown that the ligand is bridging and is attached to different potassium ions via the oxygen atom of the NO group and the quinone oxygen.

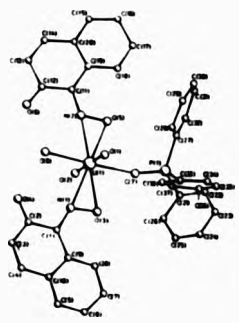


Fig. 2.2

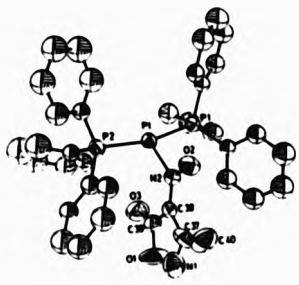


Fig. 2.3

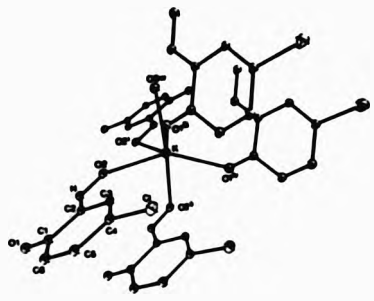


Fig. 2.4

2.3 Metal Complexes of 5-Acetylamino-1,2-benzoquinone 2-oxime

Previous studies of quinone mono-oximic complexes have involved mainly ligands having substituents without hydrophilic properties such as 4-bromo-1,2-benzoquinone 2-oxime and 5-methoxy-1,2-benzoquinone 2-oxime.[9,13] Some exceptions, involving ligands with hydrophilic substituents attached to the ring are a few complexes derived from sulphonated 1,2-naphthoquinone mono-oximes,[41-43] 5-hydroxy-1,2-benzoquinone 2-oxime and 5-acetylamino-1,2-benzoquinone 2-oxime.[44]

As noted in the introduction, one of the aims of the present work has been to investigate complexes of 5-acetylamino-1,2-benzoquinone 2-oxime which are expected to show hydrophilic properties due to the presence of the acetylated amino group. Previously only two complexes reported from 5-acetylamino-1,2-benzoquinone 2-oxime [sodium tris(5-acetylamino-1,2-benzoquinone 2-oximato)-ferrate(II) tetrahydrate and bis(5-acetylamino-1,2-benzoquinone 2-oximato)bis(pyridine)iron(II)].[44]

In this study nickel(II), copper(II), cobalt(III), and manganese(III) complexes of 5-acetylamino-1,2-benzoquinone 2-oxime have been prepared and investigated. The synthesis of these

complexes was achieved by the following two routes:

(i) The nitrosation of 3-acetylaminophenol in the presence of copper(II) sulphate pentahydrate, nickel(II) chloride hexahydrate, cobalt(II) chloride hexahydrate, sodium hexanitrocobaltate(III) or manganese(II) chloride tetrahydrate.

(ii) The direct reaction of the ligand with the metal compounds given above.

2.3.1 *Synthesis of Copper(II) Complexes of 5-Acetylamino-1,2-benzoquinone 2-oxime*

Nitrosation of 3-acetylaminophenol with sodium nitrite/acid in the presence of copper(II) sulphate pentahydrate gave a brown solid which was shown to contain two major products by t.l.c.. Separation of the mixture was achieved using Soxhlet extraction. This gave 3-acetylamino-1,4-benzoquinone 4-oxime and bis(5-acetylamino-1,2-benzoquinone 2-oximato)copper(II). The complex also resulted in almost quantitative yield when 5-acetylamino-1,2-benzoquinone 2-oxime was reacted with copper(II) chloride dihydrate in methanol.

3-Acetylamino-1,4-benzoquinone 4-oxime was characterised by elemental analysis, mixed melting point determination, and comparative i.r. and ^{1}H n.m.r. spectroscopy with an authentic sample.[44] Furthermore

during this study the structure of this compound was confirmed by X-ray crystallography (see Chapter 1).

The formulation of bis(5-acetylamino-1,2-benzoquinone 2-oximato)copper(II) was established by full elemental analysis and supported by thermal gravimetric analysis (Table 2.2) and i.r. spectroscopy.

The i.r. spectrum (Fig. 2.5) included two bands, at 3280 and 3321 cm^{-1} which are assignable to νNH of the acetyl group. Two strong bands were also observed at 1601 cm^{-1} and 1683 cm^{-1} assignable to the ring νCO of the ligand[44] and the amide CO group respectively. As noted in Chapter 1, the ring νCO in the free ligand appears at 1642 cm^{-1}. The lowering of the νCO frequency upon complexation indicates the involvement of the ring CO in bonding.

Bis(5-acetylamino-1,2-benzoquinone 2-oximato)copper(II) reacted readily at room temperature with pyridine and 2,2'-dipyridyl to give the adducts bis(5-acetylamino-1,2-benzoquinone 2-oximato)bis(pyridine)copper(II) and bis(5-acetylamino-1,2-benzoquinone 2-oximato)(2,2'-dipyridyl)copper(II). However in contrast to the analogous nickel(II) complex the copper complex failed to react with hydroxylamine.

The i.r. spectra of the adducts $Cu(5\text{-}Acqo)_2(py)_2$ and

Table 2.2 Thermal Gravimetric Analysis and Room Temperature Magnetic Moments of $Cu(5\text{-}Acqo)_2$ and its Lewis Base Adducts

Compound	Weight of sample (mg)	T(°C)[a,b]	Weight loss (mg) Found	Calc.	Decomposition Temperature (°C)[b]	μ_B
$Cu(5\text{-}Acqo)_2$	270	-	-	-	240 - 250	1.79
$Cu(5\text{-}Acqo)_2(dipy)$	184	-	-	-	220 - 240	1.79
$Cu(5\text{-}Acqo)_2(py)_2$	172	150 - 180	47	47	240 - 250	1.94

a=Temperature of the loss of pyridine, b=Maxima on the (rate of weight loss) against temperature curve.

Fig. 2.5 Infra-red Spectrum of $Cu(5\text{-}Acgo)_2$

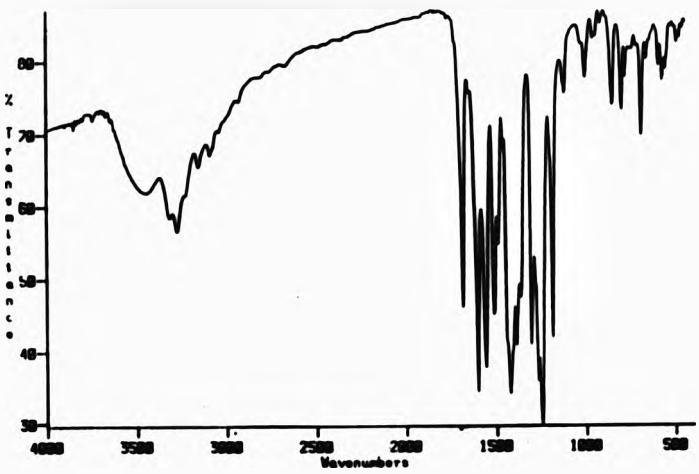


Fig 2.6 Infra-red Spectrum of $Cu(5\text{-}Acgo)_2(py)_2$

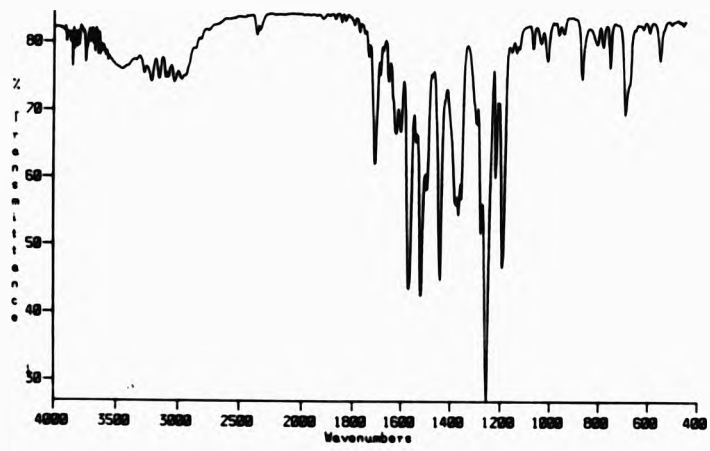
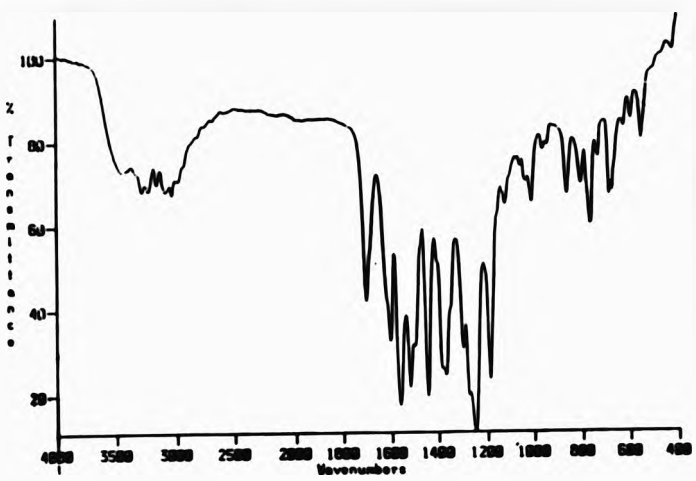


Fig 2.7 Infra-red Spectrum of $Cu(5\text{-}Acqo)_2(dipy)$



$Cu(5\text{-}Acqo)_2(dipy)_2$ (Fig 2.6 and Fig 2.7) included the expected bands due to the νCO of quinone oximic and the acetyl groups.

The formation of bis(5-acetylamino-1,2-benzoquinone 2-oximato)(2,2′-dipyridyl)copper(II) is in accord with previous reports involving reactions of other copper(II) mono-oximates with 2,2′-dipyridyl.[26,45] However the formation of a diadduct with pyridine is novel. Previously all reported adducts of $Cu(qo)_2$ complexes with pyridine were found to be 1:1 adducts.[9]

The presence of two moles of pyridine per mole of complex has been established by full elemental analysis

as well as thermal gravimetric analysis (Table 2.2) and macroscale pyrolysis. Thermal gravimetric analysis of bis(5-acetylamino-1,2-benzoquinone 2-oximato)bis-(pyridine)copper(II) gave a quantitative loss of pyridine (2 mols/1 mol of adduct) over a temperature range of 150-180 °C with the parent complex decomposing at *ca.* 250 °C. Loss of pyridine in the region 150-200 °C has also been observed in the monopyridine adducts of other copper(II) complexes of quinone mono-oximes.[9] However in the case of the bis(5-acetylamino-1,2-benzoquinone 2-oximato)-(2,2'-dipyridyl)copper(II) there was no similar loss of the base. Instead the adduct decomposed in a single step at *ca.* 240 °C. So far the formation of the bis Lewis base adducts by complexes of the type $Cu(chel)_2$ has been observed only in the case of $Cu(hfac)_2$ (hfacH = hexafluoroacetylacetone). The formation of this octahedral and isolable adduct is well established,[46,47] whereas an unstable monopyridine adduct has been reported for bis(acetylacetonato)copper(II).[48,49] In the case of bis(hexafluoroacetylacetonato)copper(II) the attachment of two pyridine ligands has been correlated with the electron withdrawing nature of the CF_3 group which enhances the electrophilic character of the metal centre.[46,50] By analogy, the formulation of the bispyridine adduct may indicate that the acetyl group reduces the electron density on the metal centre

sufficiently so as to allow the attachment of two pyridine ligands.

2.3.2 Synthesis of Nickel(II) Complexes of 5-Acetylamino-1,2-benzoquinone 2-oxime

Nitrosation of 3-acetylaminophenol in the presence of nickel(II) chloride hexahydrate gave 3-acetylamino-1,4-benzoquinone 4-oxime and an orange residue whose elemental analysis indicated the formulation bis(5-acetylamino-1,2-benzoquinone 2-oximato)nickel(II) hexahydrate, $Ni(5\text{-}Acqo)_2.6H_2O$. Macroscale pyrolysis and thermal gravimetric analysis (Table 2.3) confirmed the loss of six water molecules on heating. This orange solid was also obtained from the direct reaction of 5-acetylamino-1,2-benzoquinone 2-oxime with nickel(II) chloride hexahydrate in 1:1 water-acetic acid. In contrast the direct reaction of 5-acetylamino-1,2-benzoquinone 2-oxime with nickel(II) chloride hexahydrate in methanol afforded a brown complex, $Ni(5\text{-}Acqo)_2.nH_2O$ (n = 2-6), whose degree of hydration varied from preparation to preparation. Both the orange and brown complexes reacted with pyridine to give the same adduct, bis(5-acetylamino-1,2-benzoquinone 2-oximato)bis(pyridine)nickel(II).

Pyrolysis of the orange complex $Ni(5\text{-}Acqo)_2.6H_2O$ at 120°C / 0.1 mm gave the anhydrous complex,

Table 2.3 Thermal Gravimetric Analysis and Room Temperature Magnetic Moments of $Ni(5\text{-}Acqo)_2$ and its Lewis Base Adducts

Compound	Weight of Sample (mg)	T (°C)[a,b]	Weight Loss (mg) Found	Calc.	Decomposition Temperature (°C)[b]	μ_B
$Ni(5\text{-}Acqo)_2$	200	- -	-	-	250 - 260	1.10
$Ni(5\text{-}Acqo)_2.6H_2O$	156	100 - 120	32	31	250 - 260	2.99
$Ni(5\text{-}Acqo)_2(NH_2OH)_2$	136	140 - 220	18	19	250 - 260	3.25
$Ni(5\text{-}Acqo)_2(dipy)$	166	- -	-	-	260 - 270	2.98
$Ni(5\text{-}Acqo)_2(py)_2$	155	- -	-	-	250 - 260	3.00

a=Temperature of the loss of water and hydroxylamine, b=Maxima on the (rate of weight loss) against temperature curve.

bis(5-acetylamino-1,2-benzoquinone 2-oximato)nickel(II).

Both the hydrated and anhydrous forms of $Ni(5\text{-}Acqo)_2$ reacted readily with 2,2'-dipyridyl to give the adduct bis(5-acetylamino-1,2-benzoquinone 2-oximato)-(2,2'-dipyridyl)nickel(II). However it was found that only the anhydrous $Ni(5\text{-}Acqo)_2$ reacts with hydroxylamine at low temperature to give the hydroxylamine diadduct $Ni(5\text{-}Acqo)_2(NH_2OH)_2$. Previously, adducts of the type $Ni(\beta\text{-diket})(NH_2OH)_2$ have been prepared by the reaction of Ni(II) acetylacetonate or benzoylacetonate with hydroxylamine at 0 °C.[51]

In the i.r. spectra (Fig. 2.8 and Fig. 2.9) of $Ni(5\text{-}Acqo)_2.6H_2O$ and $Ni(5\text{-}Acqo)_2.nH_2O$, the presence of water is indicated by bands at 3572-3233 cm^{-1} and 3320-3229 cm^{-1} respectively. The expected bands due to νCO are also evident in the spectra of the hydrated complexes as well as in the spectra of the anhydrous complex (Fig 2.10) and the adducts $Ni(5\text{-}Acqo)_2(py)_2$ (Fig 2.11), $Ni(5\text{-}Acqo)_2(dipy)$ (Fig 2.12), $Ni(5\text{-}Acqo)_2(NH_2OH)_2$ (Fig 2.13).

Thermal gravimetric analysis of $Ni(5\text{-}Acqo)_2(NH_2OH)_2$ showed a quantitative loss of hydroxylamine (2 moles/1 mole of adduct) over the temperature range of 140-220 °C with the parent complex decomposing at *ca.* 260 °C. However, in the case of the $Ni(5\text{-}Acqo)_2$ adducts

Fig. 2.8 Infra-red Spectrum of $Ni(5\text{-}Acqo)_2.6H_2O$

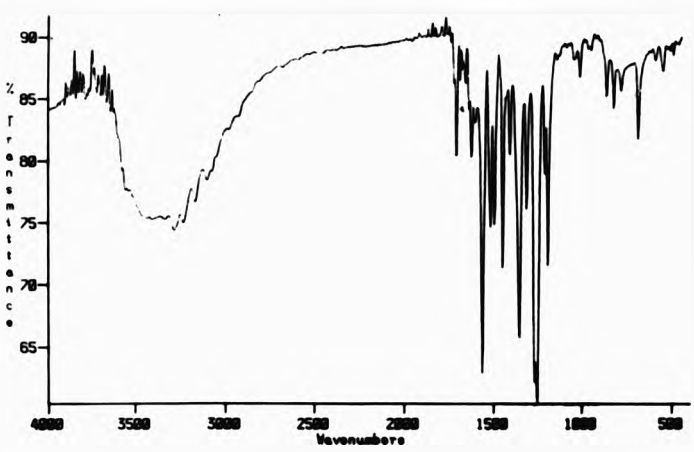


Fig. 2.9 Infra-red Spectrum of $Ni(5\text{-}Acqo)_2.nH_2O$ (n = 2- 6)

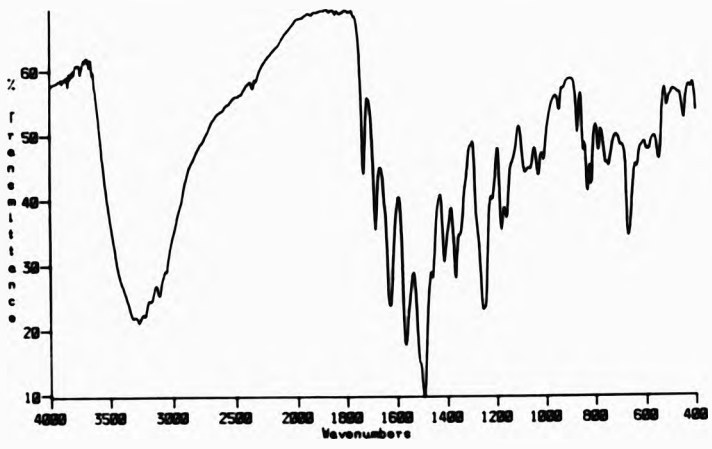


Fig. 2.10 Infra-red Spectrum of Ni(5-Acqo)$_2$.

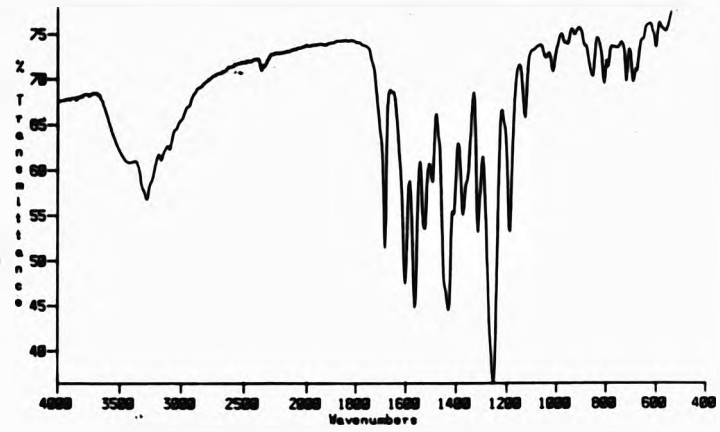


Fig. 2.11 Infra-red Spectrum of Ni(5-Acqo)$_2$(py)$_2$

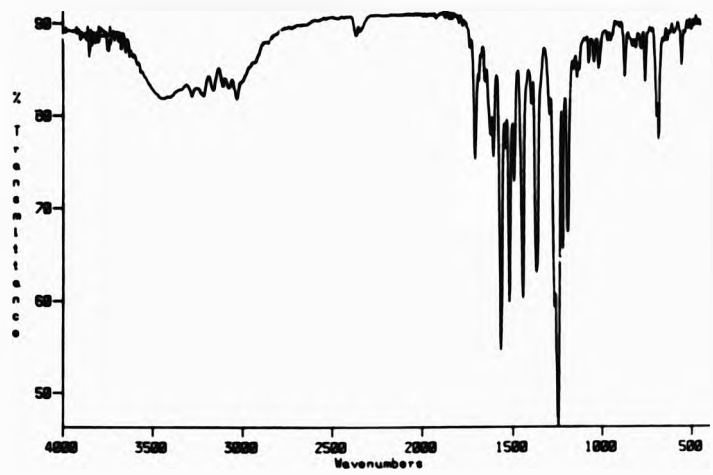


Fig. 2.12 Infra-red Spectrum of $Ni(5\text{-}Acqo)_2(dipy)$

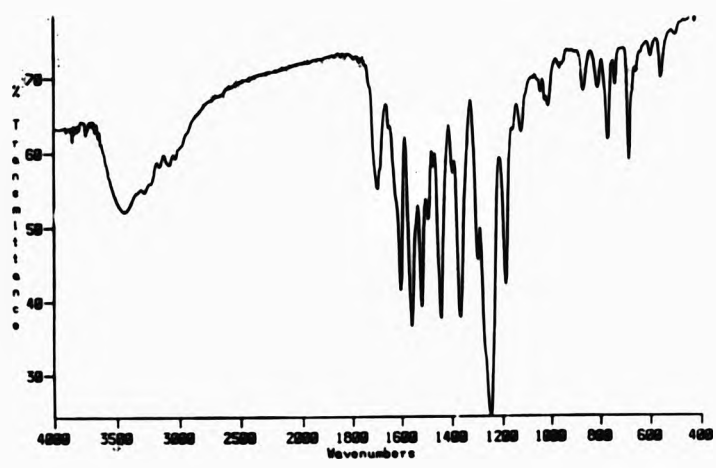
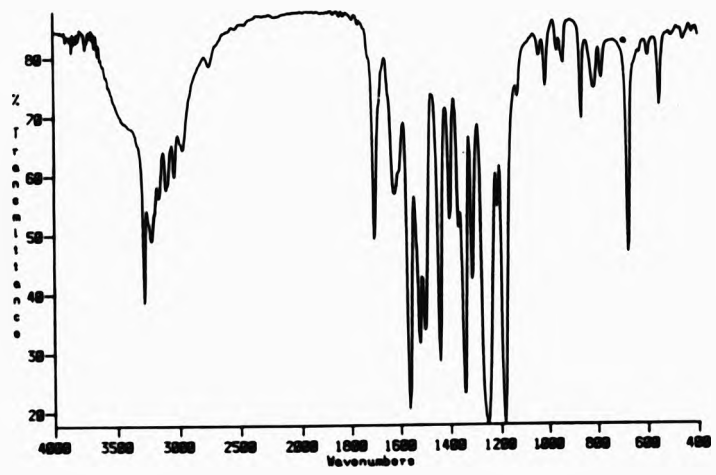


Fig. 2.13 Infra-red Spectrum of $Ni(5\text{-}Acqo)_2(NH_2OH)_2$



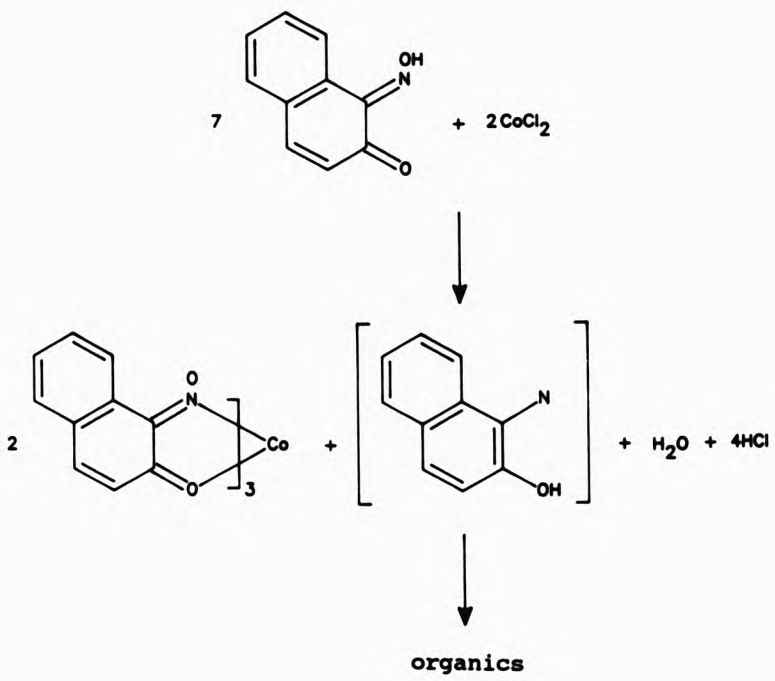
involving pyridine and 2,2-dipyridyl there was no similar loss of base, but the adducts decomposed in a single stage between 250 and 260 °C (Table 2.3).

2.3.3 Synthesis of cobalt(III) Complexes of 5-Acetylamino-1,2-benzoquinone 2-oxime

In the case of the synthesis of cobalt complexes of 5-acetylamino-1,2-benzoquinone 2-oxime three routes were investigated. Namely the direct reaction of the ligand with cobalt(II) chloride hexahydrate; the nitrosation of 3-acetylaminophenol in the presence of cobalt(II) chloride hexahydrate or sodium hexanitrocobaltate(III); and the direct reaction of the ligand with sodium hexanitrocobaltate(III).

The direct reaction of cobalt(II) chloride hexahydrate with the ligand in methanol gave a red solid as the major product together with smaller quantities of several soluble products. The elemental analysis of the red solid was in good agreement with that expected for tris(5-acetylamino-1,2-benzoquinone 2-oximato) cobalt(III), $Co(5\text{-}Acqo)_3$. This formulation which involves cobalt in oxidation state (III) was further supported by the diamagnetic character of the product and its unreactivity towards pyridine. This behaviour compares well with previous reports on the formation of cobalt(III) complexes e.g. $Co(1\text{-}nqo)_3$, from analogous

reactions involving the mono-oximes of 1,2-naphthoquinone and cobalt(II) chloride hexahydrate.[52,53] In these cases it has been suggested that oxidation of Co(II) to Co(III) involves reduction/deoxygenation of the naphthoquinone mono-oxime and that the stoichiometry of the reaction is as indicated by Reaction 2.10.[15]



Reaction 2.10

T.l.c. examination of the red solid product formulated as $Co(5\text{-}Acqo)_3$ indicated the presence of two major and

two minor components which probably correspond to isomeric forms of the complex. The presence of two or more isomers is to be expected as a trischelated cobalt(III) complex can exist in enantiomeric configurations about the metal atom (Fig. 2.14).[54] Furthermore, due to the unsymmetrical nature of the 5-AcqoH ligand, geometrical isomers (e.g. *facial* and *meridial*) can exist for each of the enantiomeric forms (Fig. 2.15).

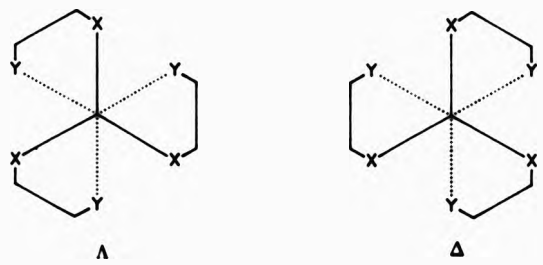


Fig. 2.14

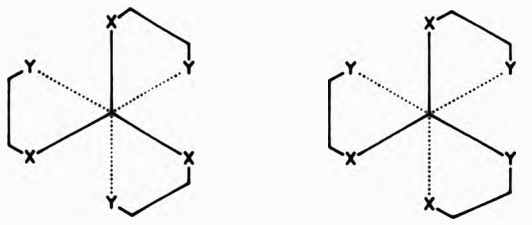


Fig. 2.15

Previously, several cobalt complexes of the type $Co(chel)_3$ (where *chel* is an unsymmetrical chelating ligand) which exhibit geometric isomerism have been reported[55,56] e.g. tris(1,1,1-trifluoro-2,4-pentanedionato)cobalt(III), tris(1-phenyl-1,3-butanedionato)cobalt(III) and tris(glycinato) cobalt(III).

When the reaction of 5-acetylamino-1,2-benzoquinone 2-oxime with cobalt(II) chloride hexahydrate was carried out in either 50% aqueous acetic acid or 50% methanolic acetic acid only two isomeric forms of tris(5-acetylamino-1,2-benzoquinone 2-oximato)-cobalt(III) resulted as indicated by t.l.c. The formulation of the product as $Co(5\text{-}Acqo)_3$ was again established by full elemental analysis, t.g.a. and i.r. spectroscopy (Fig. 2.16). In addition, in this case it was possible to obtain more information about the molecular configuration of $Co(5\text{-}Acqo)_3$ by COSY, ^{13}C and ^{1}H n.m.r. spectroscopy (see Section 2.3.5).

The nitrosation reaction of 3-acetylaminophenol in the presence of cobalt(II) chloride hexahydrate gave a mixture of 5-acetylamino-1,2-benzoquinone 2-oxime, 3-acetylamino-1,4-benzoquinone 4-oxime and a black cobalt containing product. Elemental analysis for the black product indicated the presence of five $Acqo^-$ ligands per two metals. The product had similar i.r.

Fig.2.16 Infra-red Spectrum of $Co(5\text{-}Acqo)_3$

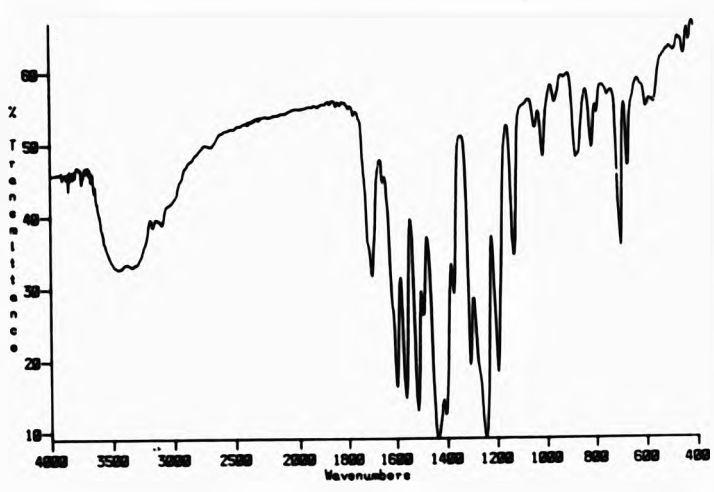
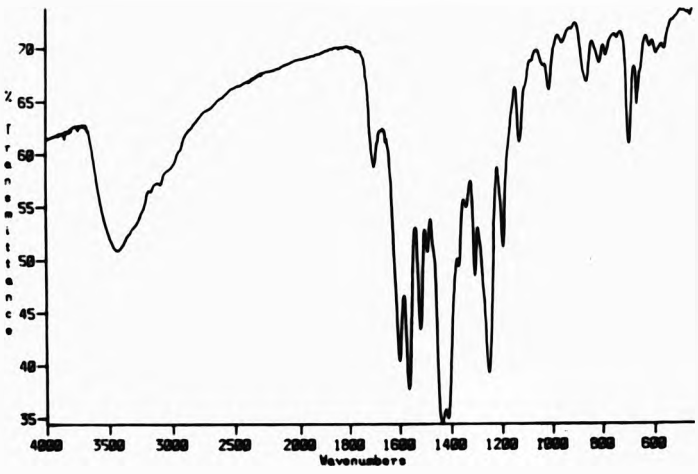


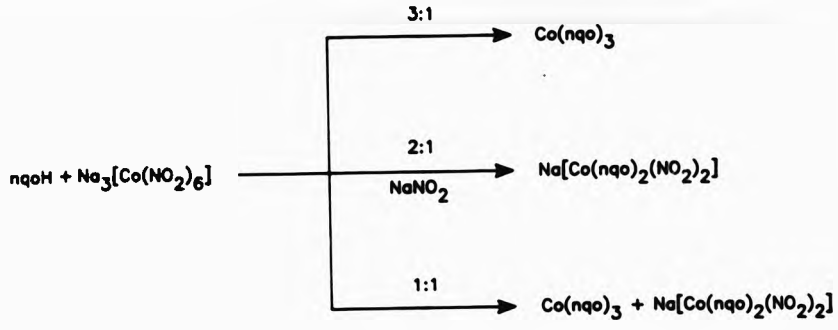
Fig. 2.17 Infra-red Spectrum of $[Co_2(5\text{-}Acqo)_5IO_2$



(Fig. 2.17) to $Co(5\text{-}Acqo)_3$, and failed to react with pyridine. On the basis of these observations the product has been tentatively formulated as penta(5-acetylamino-1,2-benzoquinone 2-oximato)-μ-peroxo-dicobaltate(III), $[Co_2(5\text{-}Acqo)_5]O_2$. Previously several dinuclear cobalt complexes containing one to three bridging groups have been reported.[57-59]

The formation of a dinuclear product from the nitrosation of 3-acetylaminophenol is in contrast to analogous reactions involving naphthols which result in the formation of $Co(nqo)_3$ and $Na[Co(nqo)_2(NO_2)_2]$.[15]

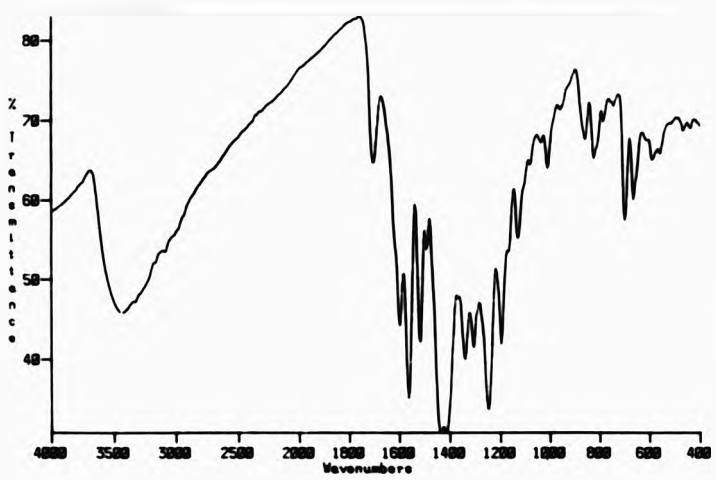
Previously, cobalt complexes of the type $Co(nqo)_3$ have also been obtained together with the complexes of the type $Na[Co(nqo)_2(NO_2)_2]$ by the interaction of the ligand with sodium hexanitrocobaltate(III).[15] In such reactions the relative ratios of the products depend on the molar amounts of the reactants (Scheme 2.1). Thus the reaction of sodium hexanitrocobaltate(III) with excess 1,2-naphthoquinone 2-oxime afforded the trischelate complex as the main product. Whereas when excess sodium hexanitrocobaltate(III) is used the main product is $Na[Co(nqo)_2(NO_2)_2]$. The yield of the sodium salt is increased when sodium nitrite is included in the reaction mixture. In line with the previous reports, the reaction of excess 5-acetylamino-1,2-benzoquinone 2-oxime with sodium hexanitrocobaltate(III) led to the



Scheme 2.1

formation of the trischelate, $Co(5\text{-}Acqo)_3$ in almost quantitative yield. In contrast to previous results, the other systems involving the reaction of 5-acetylamino-1,2-benzoquinone 2-oxime with excess sodium hexanitrocobaltate(III) in the presence of sodium nitrite gave a mixture which could not be separated. However, sodium dinitro(5-acetylamino-1,2-benzoquinone 2-oximato)cobalt(III), $Na[Co(5\text{-}Acqo)_2(NO_2)_2]$, was obtained when the phenol was nitrosated in the presence of sodium hexanitrocobaltate(III). The formation of the dinitro complex was established on the basis of its i.r. (Fig. 2.18), full elemental analysis, its diamagnetic nature and conductivity in water.

Fig. 2.18 Infra-red Spectrum of Na[Co(5-Acqo)$_2$(NO$_2$)$_2$]



2.3.4 *Synthesis of Manganese(III) Complexes of 5-Acetylamino-1,2-benzoquinone 2-oxime*

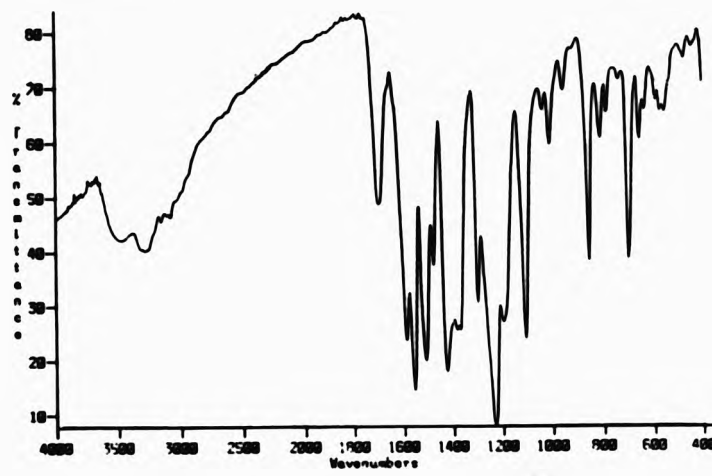
When 3-acetylaminophenol was nitrosated in the presence of manganese(II) chloride tetrahydrate in acetate buffer a green-black solid was formed. T.l.c showed this solid to contain 3-acetylamino-1,4-benzoquinone 4-oxime and another product. Elemental analysis for the latter, which remained as a residue after extracting the mixture with diethyl ether, indicated the formulation tris(5-acetylamino-1,2-benzoquinone 2-oximato) manganese(III) monohydrate. This formulation was further supported by thermal gravimetric analysis and the unreactivity of the product towards pyridine. Similar

behaviour has been observed in the case of 1-naphthol and 2-naphthol which when nitrosated in the presence of manganese(II) chloride tetrahydrate also afford the respective manganese(III) trischelate.[60] In contrast it has been found that the nitrosation under the same conditions[60] of other phenols such as 4-t-butylphenol, 4-chlorophenol and 4-methylphenol in the presence of manganese(II) chloride tetrahydrate only affords a mixture of organic products.

Manganese(II) chloride tetrahydrate showed no reaction with the ligand in methanol at 20 °C but under reflux conditions a dark solid resulted. The i.r. spectrum of this solid was ill-defined and its t.l.c. indicated the presence of a mixture of products. However when the reaction between 5-AcqoH and manganese(II) chloride tetrahydrate was carried out in the presence of ammonium buffer (pH 10) tris(5-acetylamino-1,2-benzoquinone 2-oximato)manganese(III) monohydrate, resulted in high yield.

The i.r. spectrum of $Mn(5\text{-}Acqo)_3.H_2O$ (Fig. 2.19) indicated that the C=O vibrations assignable to the amide and the quinone oximic groups occur at 1701 and 1591 cm^{-1} respectively. Two bands observed at 3485 and 3286 cm^{-1} are characteristic of νNH of secondary amides.

Fig. 2.19 Infra-red Spectrum of $Mn(5\text{-}Acqo)_2.H_2O$



2.3.5 The Structure of Copper(II), Nickel(II), Manganese(III), and Cobalt(III) Complexes of 5-Acetylamino-1,2-benzoquinone 2-oxime

Electronic spectroscopy and magnetochemical measurements have been used extensively for the study of the structure of transition metal complexes. For diamagnetic compounds n.m.r. studies have also proved useful for structural characterisation. These techniques have been used for the structural characterisation of the complexes synthesized during this study.

Quinone mono-oximes and their complexes are noted for their strong absorption in the u.v. region which tails

into the visible. This gives intense colour to the compounds, a property which has been used in analytical purposes.

The electronic spectra of $Cu(5\text{-}Acqo)_2$, $Cu(5\text{-}Acqo)_2(py)_2$, and $Cu(5\text{-}Acqo)_2(dipy)$ were found to be similar (e.g. Figs. 2.20) and their molar absorptivities are given in Table 2.4. As with other quinone oximic complexes the spectra show intense absorptions in the u.v. region which are comparable to absorptions shown by the protonated ligand (Fig. 2.21). The u.v. bands tail into the visible region and as a consequence bands due to d – d transitions appear as a broad shoulder which has a high extinction coefficient (Table 2.4). For all copper(II) compounds no structural conclusion could be drawn from the electronic spectra.

The electronic spectra of $Ni(5\text{-}Acqo)_2.6H_2O$ (Fig. 2.22) and of the adducts $Ni(5\text{-}Acqo)_2(py)_2$, $Ni(5\text{-}Acqo)_2(NH_2OH)_2$, and $Ni(5\text{-}Acqo)_2(dipy)$ were also very similar in the region 190 - 500 nm. All spectra exhibited absorptions expected from an octahedral geometry[61] and assignable to the d-d transitions $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$. As in the case of other quinone mono-oximic complexes all band have high extinction coefficient values (Table 2.5). In the case of $Ni(5\text{-}Acqo)_2.6H_2O$ the spectrum (Fig.3.23) was

Fig. 2.20 Electronic Absorption Spectrum of $Cu(5\text{-}Acgo)_2$ (9.26×10^{-5} mol dm^{-3}) in Methanol

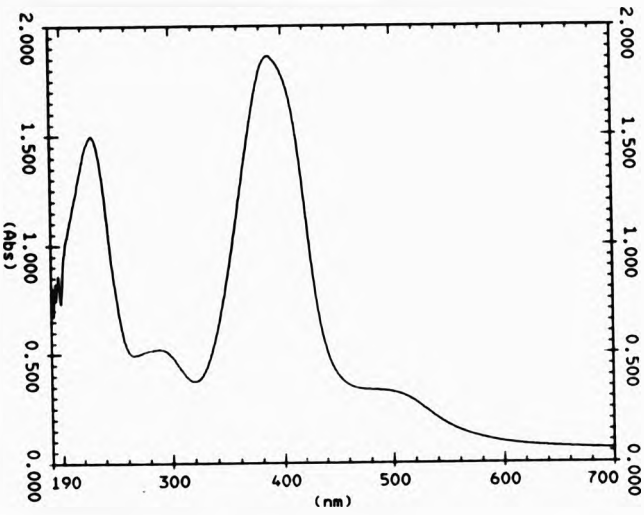


Fig. 2.21 Electronic Absorption Spectrum of 5-AcgoH (1.67×10^{-4} mol dm^{-3}) in Methanol

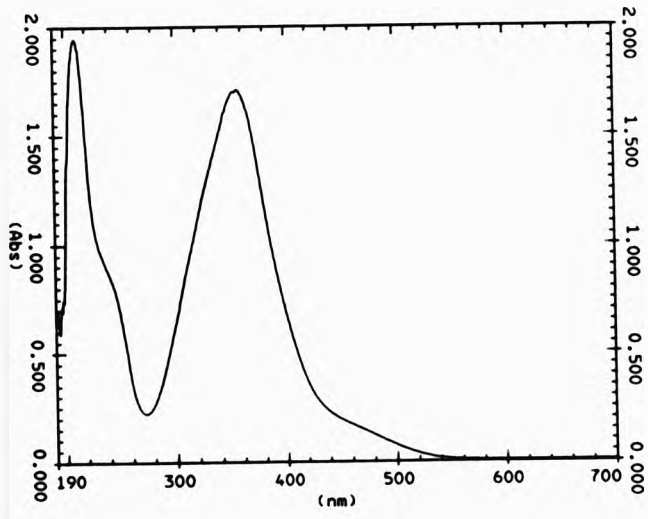


Table 2.4 Electronic Absorption Results for $Cu(5\text{-}Acqo)_2$ $Cu(5\text{-}Acqo)_2(py)_2$, $Cu(5\text{-}Acqo)_2(dipy)$, and 5-AcqoH In Methanol

Complex Concentration (mol dm^{-3})	λ_{max} nm	ϵ m^2 mol^{-1}
$Cu(5\text{-}Acqo)_2$	491	375
9.26×10^{-5}	388	2011
	279	553
	230	1614
$Cu(5\text{-}Acqo)_2(py)_2$	509	537
6.55×10^{-5}	391	3377
	292	710
	228	2976
$Cu(5\text{-}Acqo)_2(dipy)$	500	377
7.43×10^{-5}	384	2922
	310	1221
	290	1587
	229	3573
5-AcqoH	355	10204
1.67×10^{-4}	244	4796
	210	11641

also recorded at high concentration. The latter showed a band at 900 nm which is assignable to the d-d transition, $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$.

Fig. 2.22 Electronic Absorption Spectrum of $Ni(5\text{-}Acgo)_2.6H_2O$ (3.82 X 10^{-5} mol dm^{-3}) in Methanol

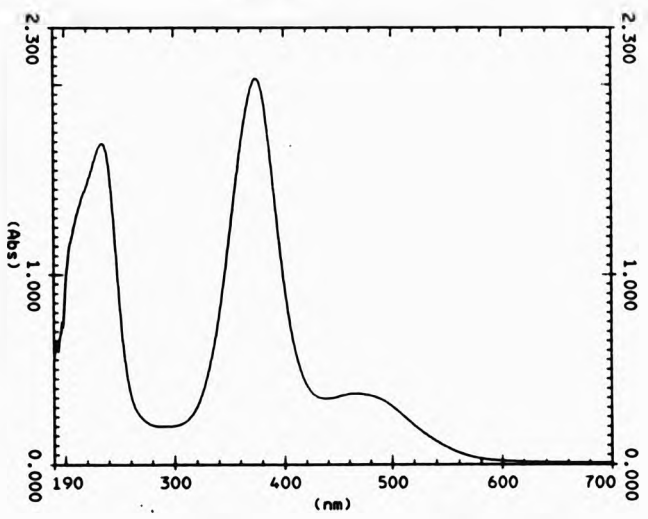


Fig. 2.23 Electronic Absorption Spectrum of $Ni(5\text{-}Acgo)_2.6H_2O$ (1.97 X 10^{-3} mol dm^{-3}) in Methanol

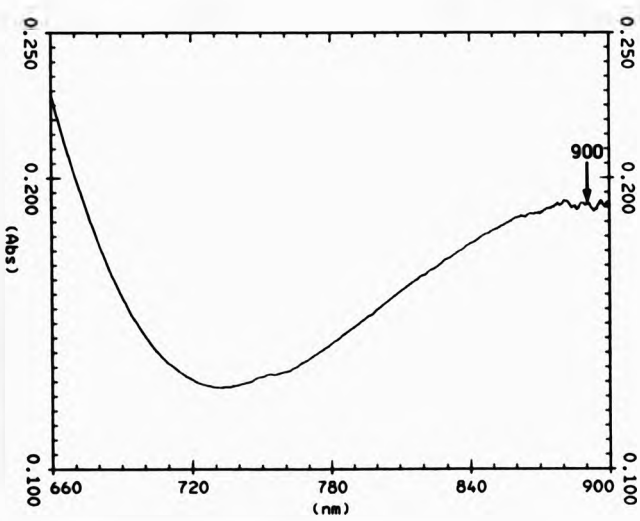


Table 2.5 Electronic Absorption Results for $Ni(5\text{-}Acqo)_2.6H_2O$, $Ni(5\text{-}Acqo)_2(py)_2$, $Ni(5\text{-}Acqo)_2(dipy)$ and $Ni(5\text{-}Acqo)_2(NH_2OH)_2$ in Methanol

Compound Concentration (mol dm^{-3})	λ_{max} nm	ϵ $m^2\ mol^{-1}$
$Ni(5\text{-}Acqo)_2.6H_2O$	485	922
3.82×10^{-5}	376	5335
	233	4440
1.97×10^{-3}	900	10
$Ni(5\text{-}Acqo)_2(py)_2$	468	766
8.00×10^{-5}	375	4232
	238	3626
$Ni(5\text{-}Acqo)_2(NH_2OH)_2$	468	434
8.26×10^{-5}	370	3607
	214	3808
$Ni(5\text{-}Acqo)_2(dipy)$	465	711
7.16×10^{-5}	375	3822
	300	1705
	290	1535
	238	4330

Manganese(III) has d^4 configuration, which can lead to either a triplet ($^3T_{1g}$) or a quintet (^5E_g) ground state. Several spin-allowed transitions are possible for the triplet ground state. In contrast only one spin-allowed

Fig. 2.24 Electronic Absorption Spectrum of $Mn(5\text{-Acqo})_3.H_2O$ (1.86 X 10^{-5} mol dm^{-3}) in Methanol

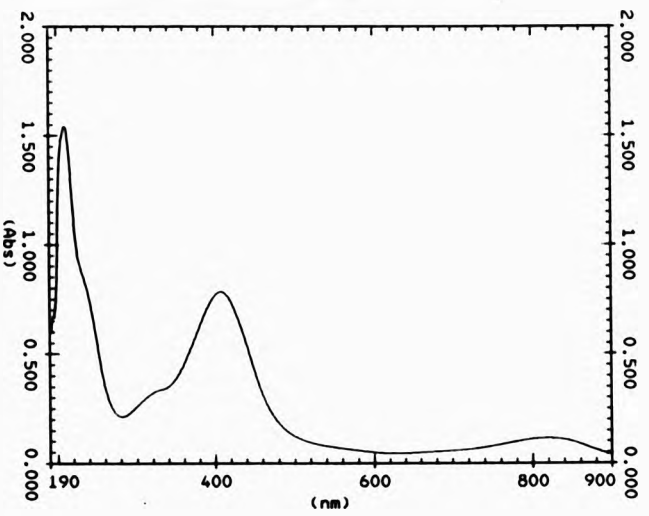


Fig. 2.25 Electronic Absorption Spectrum of $Mn(5\text{-Acqo})_3.H_2O$ (2.29 X 10^{-4} mol dm^{-3}) in Methanol

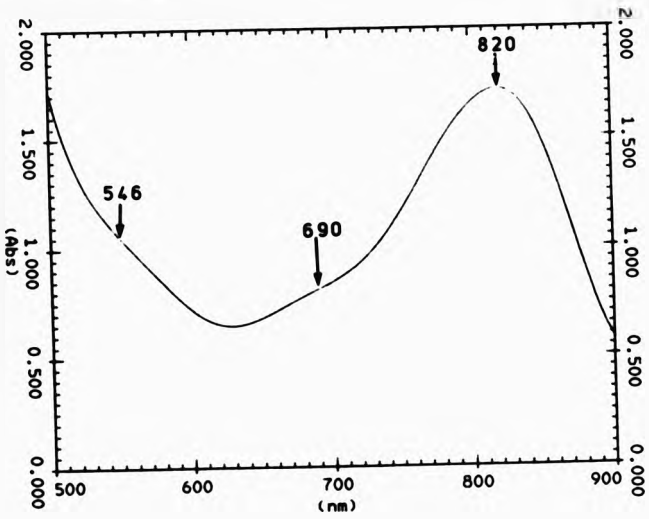


Table 2.6 Electronic Absorption Results for $Mn(5\text{-Acqo})_3.H_2O$ in Methanol

Compound Concentratio (mol dm^{-3})	λ_{max}	ϵ $m^2\ mol^{-1}$
$Mn(5\text{-Acqo})_3.H_2O$	820	608
1.86×10^{-5}	408	4210
	330	1801
	230	4747
	210	8285
$Mn(5\text{-Acqo})_3.H_2O$	820	751
2.29×10^{-4}	690	353
	546	470

transition is possible for the ^5E_g ground state.[62] The electronic spectrum (Fig. 2.24 and 2.25) for $Mn(5\text{-Acqo})_3$ consists of two intense ligand bands at 210 and 408 nm and d-d bands at 546, 690, and 820 nm. The number of d-d bands points towards the triplet ground state ($^3T_{1g}$). Molar absorptivities of $Mn(5\text{-Acqo})_3.H_2O$ are given in Table 2.6.

In their electronic spectra, low spin d^6 octahedral cobalt complexes exhibit two spin allowed transitions due to $^1A_{1g} \longrightarrow {}^1T_{1g}$ and $^1A_{1g} \longrightarrow {}^1T_{2g}$.[63] In the spectrum of $[Co(H_2O)_6]^{3+}$ these absorptions have been observed at 602 and 402 nm respectively.[63] The complexes, $Na[Co(5\text{-Acqo})_3(NO_2)_2]$ and $[Co_2(5\text{-Acqo})_5]O_2$

Fig. 2.26 Electronic Absorption Spectrum of $Na[Co(5\text{-}Acgo)_2(NO_2)_2]$ (3.12×10^{-5} mol dm^{-3}) in Methanol

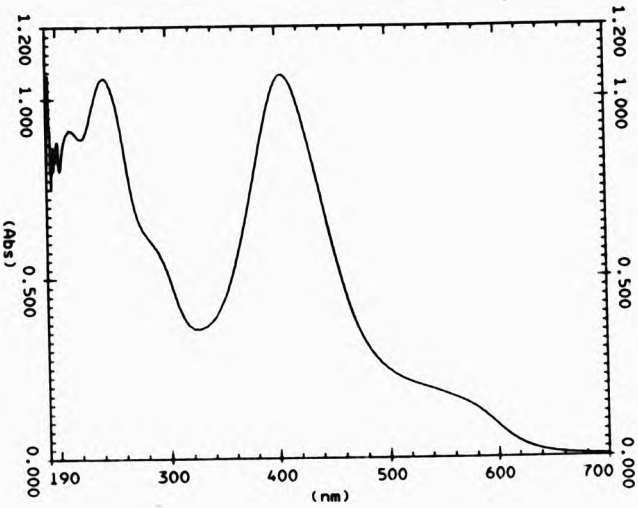


Fig. 2.27 Electronic Absorption Spectrum of $Co(5\text{-}Acgo)_2$ (2.11×10^{-5} mol dm^{-3}) in Methanol

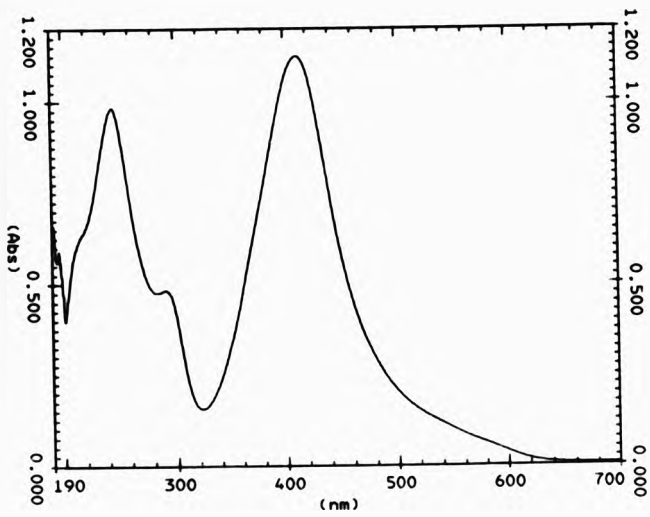


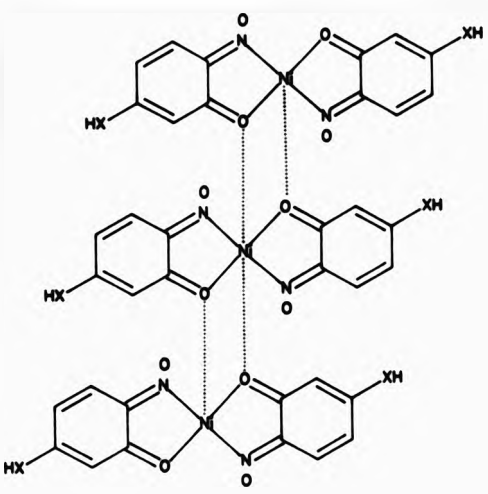
Table 2.7 Electronic Absorption Results for $Na[Co(5\text{-}Acqo)_2(NO_2)_2]$, $[Co(5\text{-}Acqo)_2]O_2$, and $Co(5\text{-}Acqo)_3$ in Methanol

Compound Concentration (mol dm^{-3})	λ_{max}	ϵ $m^2\ mol^{-1}$
$Na[Co(5\text{-}Acqo)_2(NO_2)_2]$	575	471
3.12×10^{-5}	405	3413
	285	1926
	245	3381
	210	2910
$[Co_2(5\text{-}Acqo)_2]O_2$	560	544
7.33×10^{-5}	405	2766
	285	1627
	242	2725
	210	2478
$Co(5\text{-}Acqo)_3$	412	532
2.11×10^{-5}	290	2280
	245	4654
	210	2749

have similar spectra (e.g. Fig. 2.26) which show two d-d transition bands at 575 nm and 405 nm assignable to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ respectively. In the case of $Co(5\text{-}Acqo)_3$ (Fig 2.27) the former absorption is not observed. Molar Absorptivities of $Na[Co(5\text{-}Acqo)_2(NO_2)_2]$, $[Co_2(5\text{-}Acqo)_2]O_2$, and $Co(5\text{-}Acqo)_3$ are given in Table 2.7.

Magnetically dilute copper(II) complexes have room temperature magnetic moments in the range 1.72 - 2.20 μ_B.[64,65] The room temperature magnetic moments of the complex $Cu(5\text{-}Acqo)_2$ and its adducts were found to be in the range 1.79 - 1.94 μ_B. This indicates that the compounds are magnetically dilute and hence monomeric but does not allow unambiguous structural assignments. Previously,[9] similar magnetic moments have been obtained for other copper(II) quinone oximic complexes such as $Cu(4\text{-}Clqo)_2$, $Cu(4\text{-}Brqo)_2$, $Cu(4Me\text{-}qo)_2$, $Cu(5\text{-}MeOqo)_2$ and $Cu(1\text{-}nqo)_2$.

The room temperature magnetic moments of $Ni(5\text{-}Acqo)_2.6H_2O$, $Ni(5\text{-}Acqo)_2.nH_2O$ (n = 2 - 6), $Ni(5\text{-}Acqo)_2(py)_2$, $Ni(5\text{-}Acqo)_2(dipy)_2$, $Ni(5\text{-}Acqo)_2(NH_2OH)_2$, lie between 3.0-3.3 μ_B (Table 2.3) which are within the range expected for six coordinated nickel(II).[12] This indicates that the compounds are magnetically dilute with the nickel atom in an octahedral environment. In contrast the room temperature magnetic moment of the anhydrous complex, $Ni(5\text{-}Acqo)_2$, was found to be subnormal (1.1 μ_B). The subnormal magnetic moment of $Ni(5\text{-}Acqo)_2$ can be accounted for in terms of association (Fig. 2.28) and antiferromagnetic interaction between adjacent nickel atoms as suggested previously for the related complexes of $Ni(1\text{-}nqo)_2$ and $Ni(2\text{-}nqo)_2$.[12]



X = $NCOCH_3$

Fig. 2.28

The room temperature magnetic moment of the complex $Mn(5\text{-}Acqo)_3.H_2O$ was found to be 2.88 μ_B which is close to the spin only magnetic moment (2.83 μ_B) expected for the spin paired manganese(III) in an octahedral environment. So far only a few examples of spin paired manganese(III) complexes have been reported. These include $Mn(1\text{-}nqo)_3$, $Mn(2\text{-}nqo)_3$[60] and tris(dimethylaminotroponiminato)manganese(III)[66] whose room temperature magnetic moments are 2.75, 2.70, and 3.12 μ_B.

All cobalt complexes were found to be diamagnetic in accord with their formulation as octahedral cobalt(III) complexes. The diamagnetism of the cobalt(III) complexes and low spin d^6 configuration of the manganese(III)

complex are indicative of the strong field character of 5-acetylamino-1,2-benzoquinone 2-oxime, a feature which has also been observed for other quinone oximic ligands.[60]

In the case of $Co(5\text{-}Acqo)_3$ it was possible to obtain more information about its molecular configuration by COSY ^1H and ^{13}C n.m.r. spectroscopy.

Initially the ^1H n.m.r. spectrum (Fig. 2.29) of $Co(5\text{-}Acqo)_2$ was recorded in d_6-dimethylsulphoxide at 270 MHz. This spectrum indicated the presence of three different aromatic hydrogen environments with the methyl protons of the acetyl groups appearing as a single broadened resonance. However, the number of lines in the aromatic region was not sufficient to account for the expected ortho and meta couplings. Consequently, a COSY spectrum (Fig. 2.30) of the product was recorded in order to determine the spectral assignment for the aromatic protons.

The COSY spectrum indicated that the aromatic hydrogens corresponding to the set of peaks I and III are coupled to those in the set II. Again broadening and overlapping of lines in the latter prevented the unambiguous assignment of the aromatic protons. The ^1H n.m.r. spectrum of $Co(5\text{-}Acqo)_3$ was then run at 500 MHz. This spectrum (Fig. 2.31) was found to be better resolved and

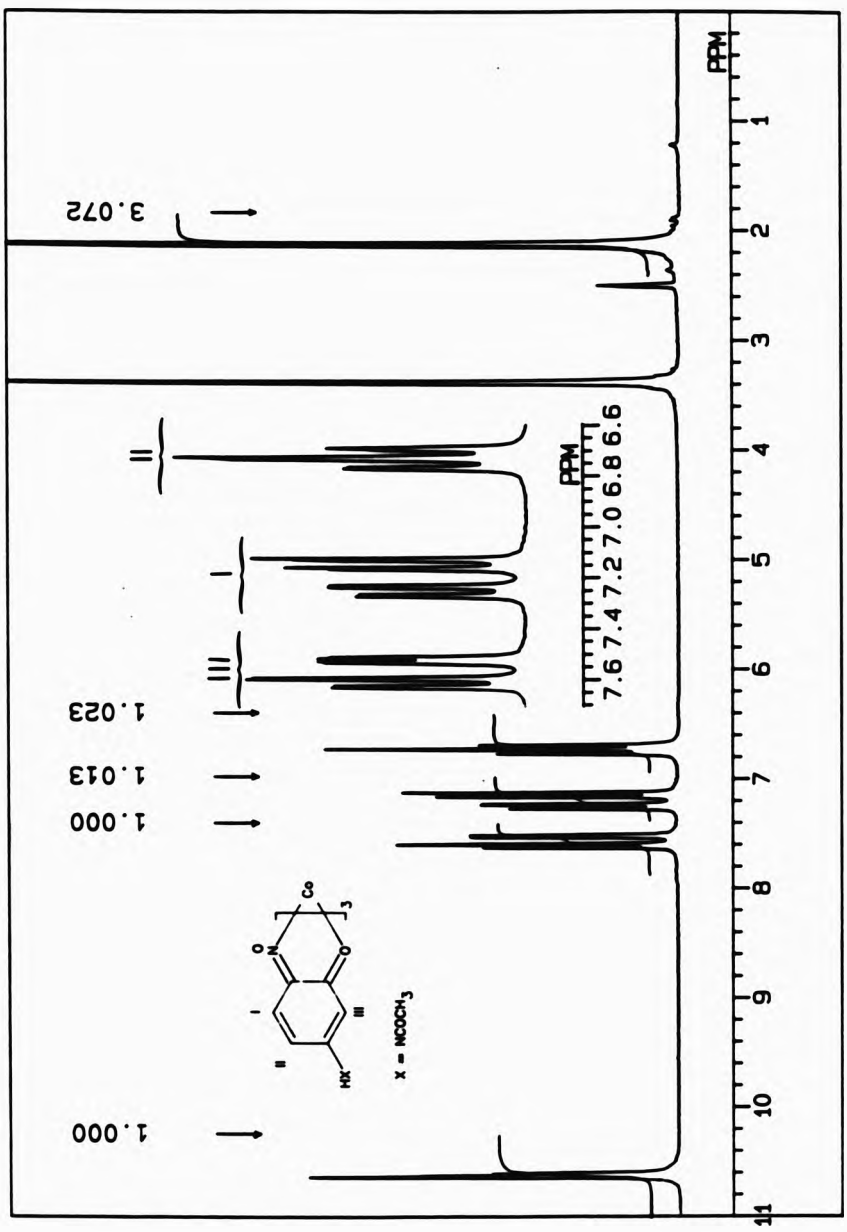
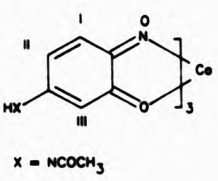
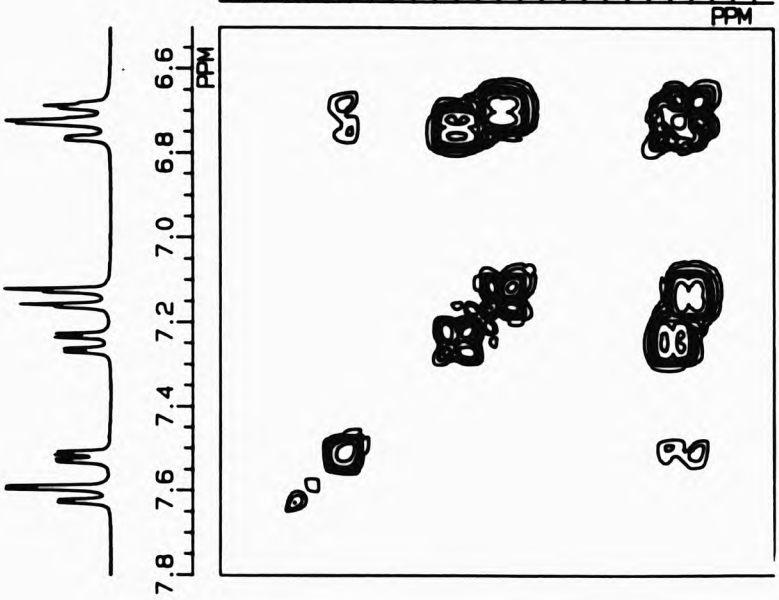


Fig. 2.29 ^{1}H Nuclear Magnetic Resonance Spectrum of Co(5-AcgO)$_3$ in d$_6$-DMSO at 270 MHz

Fig. 2.30 COSY Spectrum of $Co(5\text{-}Acqo)_3$ in d_6-DMSO at 270 MHz





pointed towards four different proton environments in the aromatic region. Preliminary examination showed the presence of eight lines in each of the sets I and III and that of fourteen lines in set II. However, further decoupling experiments (Fig. 2.32) revealed the presence of sixteen lines in the second set and thus accounting for all the expected ortho and meta couplings. As noted earlier the unsymmetrical nature of 5-AcqoH in $Co(5\text{-}Acqo)_3$ could result in the formation of *facial* and *meridial* isomers. Further more the *facial* isomer has a three fold rotation axis where as the *meridial* isomer has no symmetry. Therefore in the *facial* isomer all three chelate rings are in identical environments, while in the *meridial* isomer all three chelate rings are in different environments. Thus in the ^1H n.m.r. of the *facial* isomer all three aromatic hydrogens (say at position A in Fig. 2.33) should exhibit a doublet resonance, while those corresponding to the *meridial* form would be expected to appear as three separate doublets. Previously, examination of ^1H n.m.r. spectra of several metal trischelate complexes with bidentate unsymmetrical ligands (e.g. benzoylacetone) has shown that in the *meridial* isomers (e.g. Fig. 2.15) all three chelate rings are in different environments.[55] Therefore, In the spectrum (Fig. 2.33) of the $Co(5\text{-}Acqo)_3$, the observation of four different environments is consistant with the presence of a mixture of *facial* and *meridial* isomers. A comparison of

Fig. 2.31 ^{1}H Nuclear Magnetic Resonance Spectrum of $Co(5\text{-}Acqo)_3$ in d_6-DMSO at 500 MHz

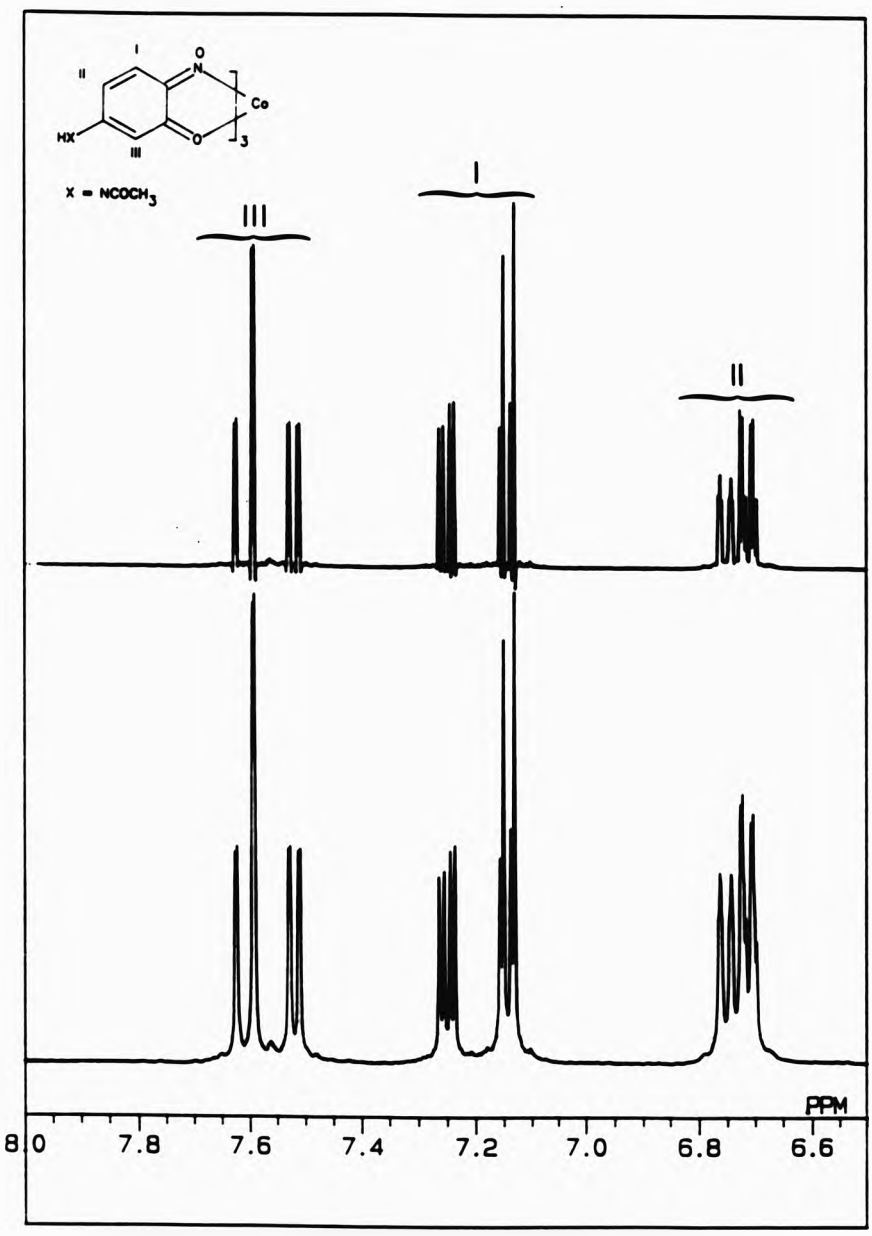


Fig 2.32 Off Resonance Decoupling Experiments for Co(5-Acac)$_3$ in d_6-DMSO

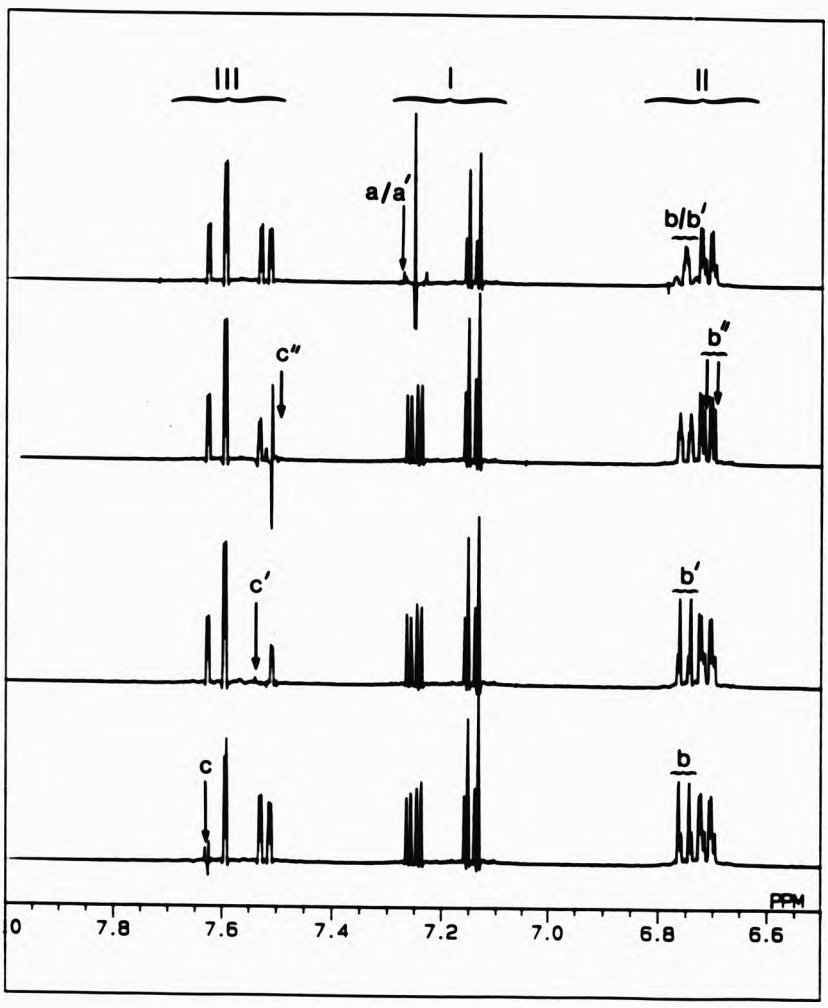
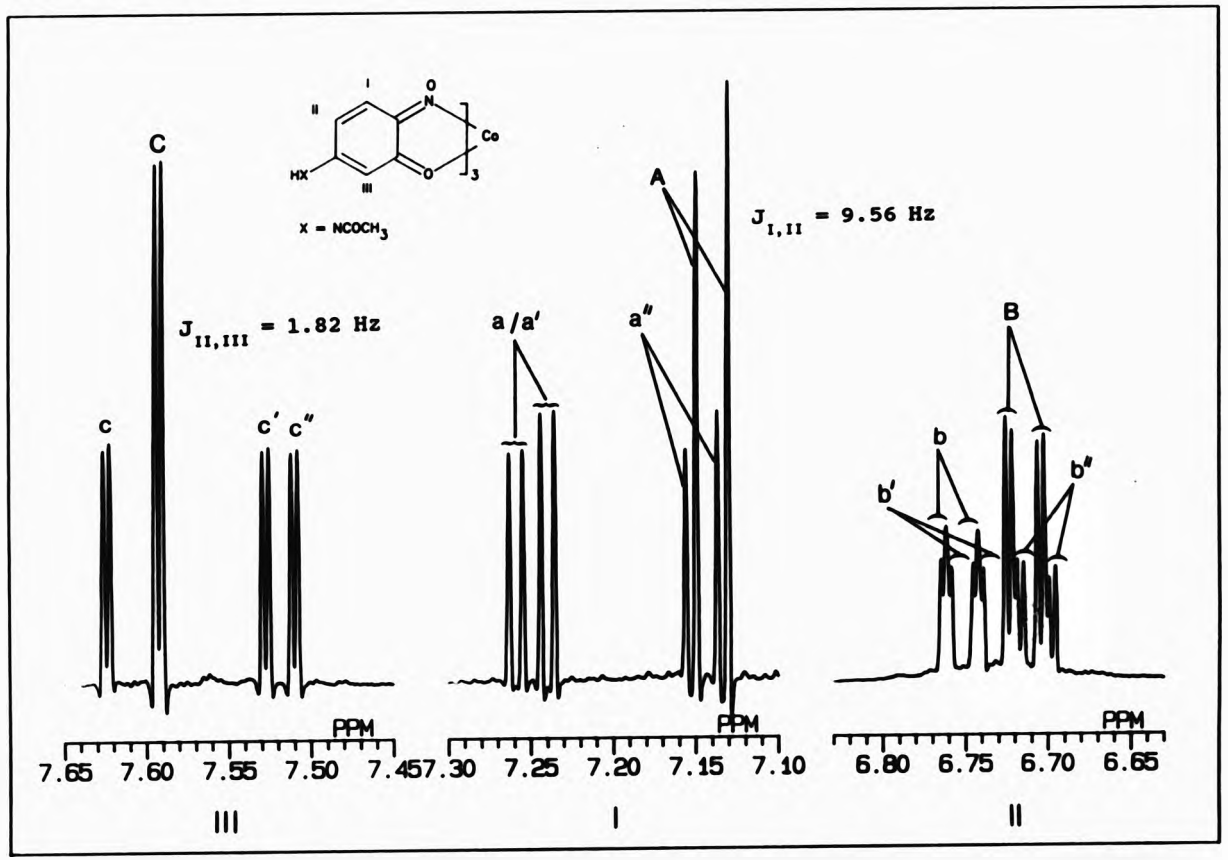


Fig. 2.33 ^{1}H Nuclear Magnetic Resonance Spectrum of $Co(5\text{-}Acqo)_3$ at 500 MHz with Assignments

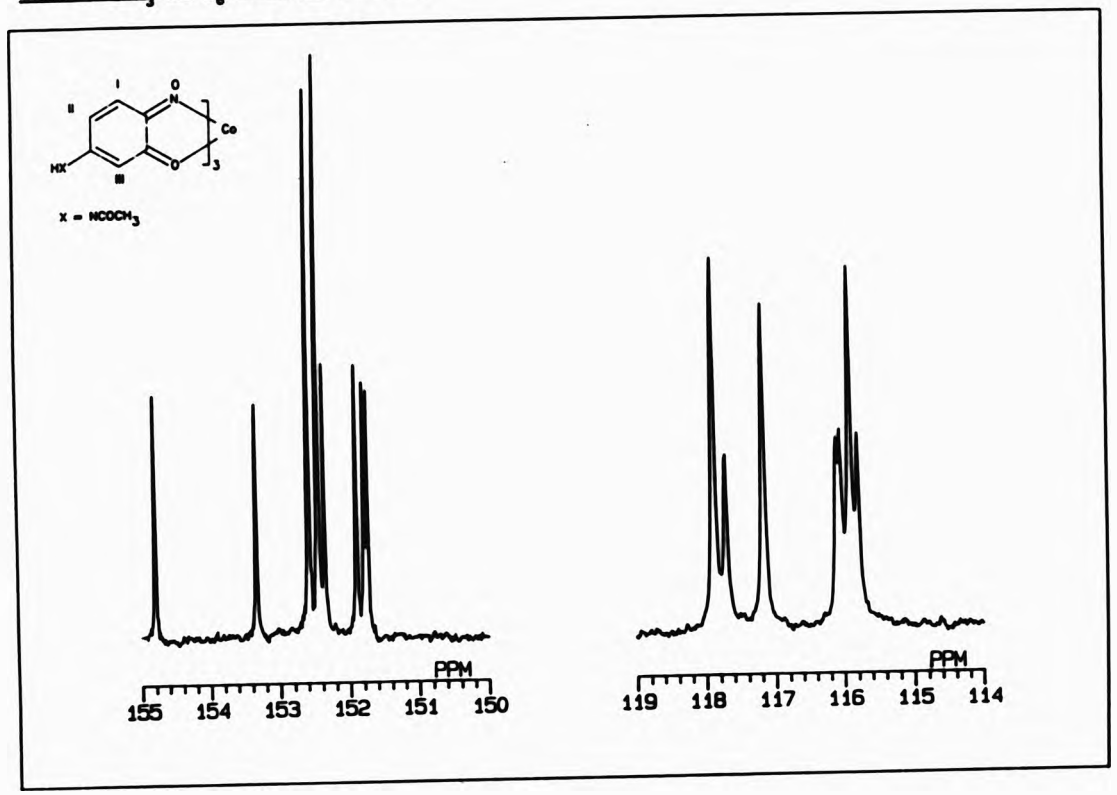


the intensity of the peaks also shows that one set has approximately twice the intensity of the remaining three. Thus the resonances at A, B and C in Fig. 2.33 were assigned to the *facial* isomer and the remaining peaks in each set were assumed to correspond to the *meridial* isomer. off resonance decoupling experiments (Fig. 2.32) allowed the assignment of all protons in the *meridial* isomer as presented in Fig. 2.33. The integration pattern (Fig. 2.33) shows that 56% of the mixture consists of the *meridial* isomer. This result is consistant with previous findings[55] which on the basis of the lower dipole moment of the *meridial* isomer had shown it to be the more stable form. An examination of the ^{1}H n.m.r. of $Co(5\text{-}Acqo)_3$ over the temperature range of 20-80 °C showed no interconversion of the isomeric forms. This observation further substantiates the stability of the *meridial* isomer and is consistant with previous results for related systems.[55]

The broad band decoupled ^{13}C n.m.r. (Fig. 2.34 and 2.35) also confirms the presence of *facial* and *meridial* isomers as it shows peaks corresponding to four different quinonoid (>C=O) carbons. The peaks for the quinonoid carbons were assigned by comparison with chemical shift data for similar compounds.[44,67]

Fig. 2.34 ^{13}C Nuclear Magnetic Resonance Spectrum of Co(5-Accol)$_3$ in d_6-DMSO at 270 MHz

Fig. 2.35 An Expansion (114-155 ppm) of ^{13}C Nuclear Magnetic Resonance Spectrum of Co(5-Acqo)$_3$ in d_6-DMSO at 270 MHz



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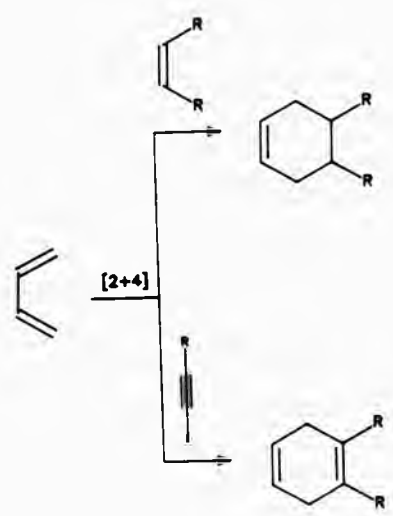
CHAPTER THREE

Addition Reactions of Complexes of Quinone Mono-oximes and the Single Crystal X-Ray Structure of 6-Bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one

3.1 Diels-Alder Reactions and other Types of Nucleophilic Addition Reactions

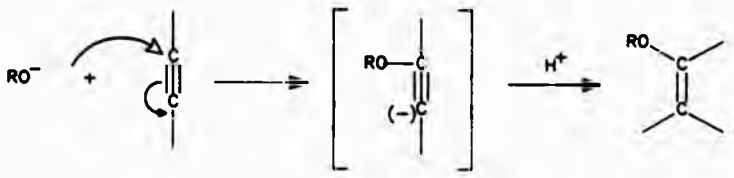
Diels-Alder reactions are [4 + 2] nucleophilic cycloaddition reactions of *dienes* or *heterodienes*, containing *1,3 cisoid diene bonding*, to activated ethylenic or acetylenic compounds known as *dienophiles*.[1,2] In general terms Diels-Alder reactions which are also known as *diene synthesis* may be presented by Scheme 3.1.



Scheme 3.1

These reactions involve the nucleophilic addition of the diene or the heterodiene, at the [1,4] position to the ethylenic or acetylenic multiply bonded carbon atoms and lead to the formation of carbocyclic or heterocyclic six membered adducts with a new multiple bond. Therefore in Diels-Alder reactions compounds which have their multiple bonds activated by conjugation with electron withdrawing substituents (e.g. CO_2R) serve as good dienophiles. Hence, ethylenic compounds such as maleic anhydride and acetylenic compounds such as dimethyl acetylenedicarboxylate and methyl propiolate are good dienophiles. Tetracyanoethylene is the most reactive dienophile discovered to date.[3] Similarly dienes or heterodienes show increased reactivity if substituted with electron donating groups (e.g. Me, MeO, Ph).

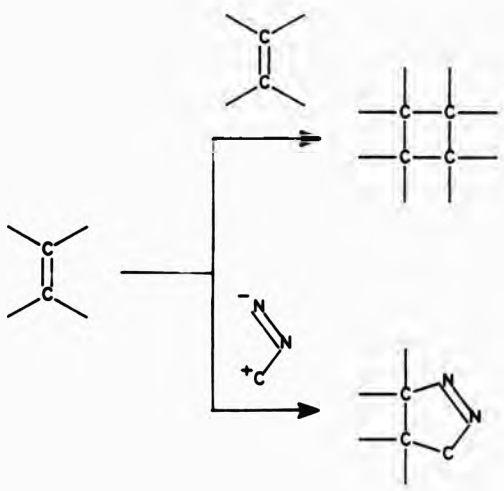
Nucleophilic additions, involve addition of a nucleophile known as the donor, to an ethylene or acetylene known as the acceptor (Scheme 3.2).[4,5,6]



Scheme 3.2

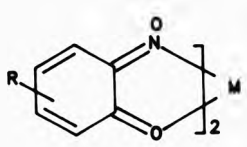
Nucleophilic additions which involve addition of a carbanion to an ethylenic or acetylenic substrate are known as *Michael reactions*. All other nucleophilic additions which follow the Michael reaction mechanism are known as *Michael type reactions*.

Other types of cycloadditions are those of [2 + 2] and [2 + 3] additions.[2,4,7] The former which involves addition between two ethylenes, is a photochemically initiated reaction and leads to the formation of a four membered ring. Whereas the latter reaction involves addition of 1,3-dipolar compounds to an ethylenic substrate and leads to the formation of a five membered ring. These reactions may be generally presented by Scheme 3.3.

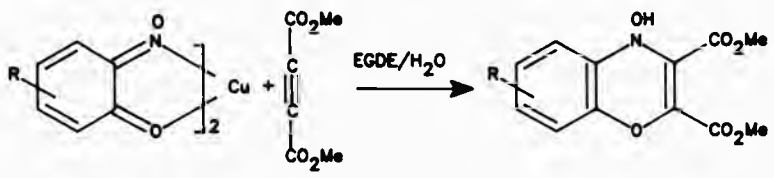


Scheme 3.3

Quinone oximato complexes (1) have diene and heterodiene character and in principle are expected to undergo Diels-Alder reactions and nucleophilic addition reactions. Diels-Alder adducts involving the heterodiene part of the complexes (1, M = Cu) have been isolated from their reaction with dimethyl acetylenedicarboxylate (e.g. Reactions 3.1 and 3.2).[8-10]

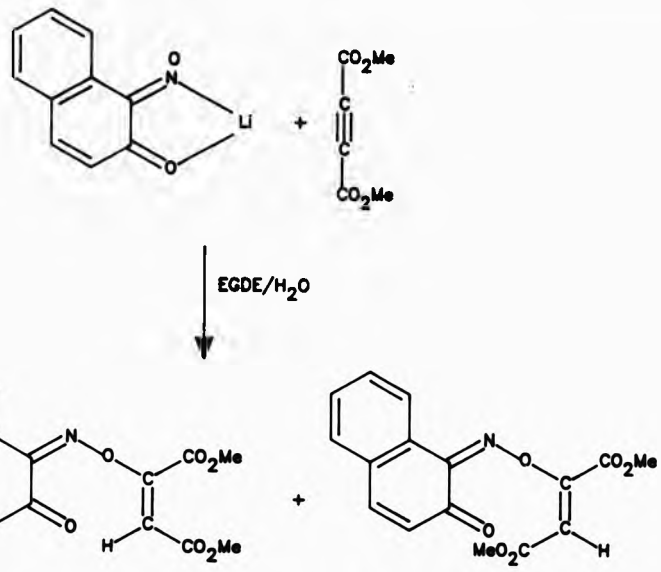


(1)



(2)

Reaction 3.1



Reaction 3.2

3.2. Previous Studies of the Reactions of the Metal Complexes of Quinone Mono-Oximes with Dimethyl Acetylenedicarboxylate

The first study of the reactions of copper(II) complexes of 1,2-quinone mono-oximes with dimethyl acetylenedicarboxylate was reported in 1976 (Reaction 3.1).[8] The systems examined are shown in Table 3.1. It was established that these reactions occur readily in aqueous ethylene glycol dimethyl ether and that the presence of water is essential. However the role of water was not established. The reactions involve

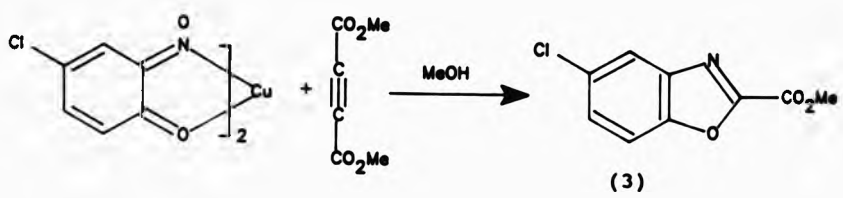
Table 3.1 Reactions of the $Cu(qo)_2$ with DMAD (Systems Examined and Results Reported in the First Study)[8]

$Cu(qo)_2$ qoH	Organic Product [1,4-Oxazine (2)] Yield (%)	M.p. (°C)
4-MeqoH	98	186-187
4-ClqoH	93	186-188
4-BrqoH	92	196-197
5-MeOqoH	96	181-183
$5\text{-}Me_2NqoH$	61	170-172
1-nqoH	91	159-160
2-nqoH	72	163-164

the heterodiene part of the complex and lead to 1,4-oxazine (2) formation. The presence of a copper containing residue was also noted. In contrast no reaction was observed with the free ligands 5-methoxy-1,2-benzoquinone 2-oxime, 1,2-naphthoquinone 1-oxime and 1,2-naphthoquinone 2-oxime, their methyl ethers or with their cobalt(III) complexes. These observations were accounted for in terms of (i) the coordinative unsaturation of copper in the $Cu(qo)_2$ complexes, (ii) the polarising ability of the metal which causes electron density shift towards the heterotermini of the ligand and (iii) the ability of the metal to participate in bonding with the triple bond of the dienophile.

Subsequently other workers[9] reinvestigated the reaction of bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) with dimethyl acetylenedicarboxylate in a mixture of ethylene glycol dimethyl ether and water and confirmed the earlier findings. However later they reported, that the analogous reaction of bis(4-chloro 1,2-benzoquinone 2-oximato)(2,2-dipyridyl)copper(II), whose octahedral[10] structure has been established by X-ray crystallography, also leads to 1,4-oxazines. Therefore contrary to the earlier suggestions coordinative unsaturation of the metal is not a requirement for the reaction.

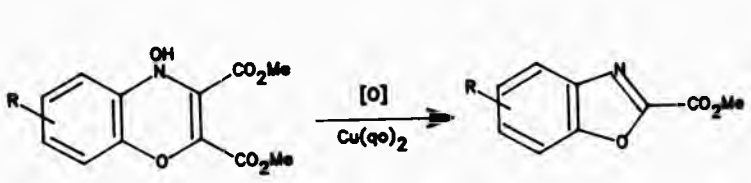
When the reaction of bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) with the dienophile was carried out in anhydrous methanol, a 1,3-oxazole (3) rather than a 1,4-oxazine (2) resulted (Reaction 3.3).[9] An unidentified copper containing solid was also isolated, which was suggested to involve copper(I). The formation of the oxazole was accounted for in terms of reduction of copper(II) to copper(I) via a deoxygenation route analogous to that suggested for the $Cu(qo)_2/Ph_3P$ system.[12] However no mechanistic details were given.



(3)

Reaction 3.3

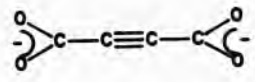
A reexamination of the reaction of bis(4-chloro-1,2-benzoquinone 2,oximato)copper(II) with the dienophile showed that in anhydrous methanol the reaction leads to the 1,4-oxazine, and not the 1,3-oxazole.[10] It was proposed that the oxazole arises from the oxazine via an oxidation process catalysed by the $Cu(qo)_2$ complex (Reaction 3.4).



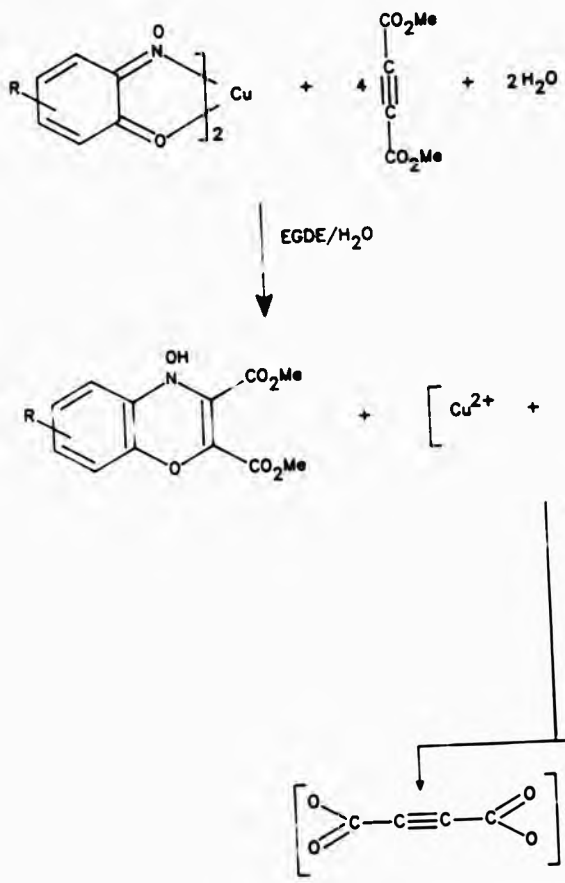
Reaction 3.4

Studies in these laboratories showed that the metal containing solid arising from the reaction of $Cu(nqo)_2$ (nqoH = 1-nqoH or 2-nqoH) complexes with dimethyl acetylenedicarboxylate in aqueous ethylene glycol dimethyl ether is the hydrated copper(II) complex of the butynedioate dianion (4).[10,13] These studies also indicated that water participates in these reactions as a reagent providing the proton necessary to the oxazine formation (Scheme 3.4). The OH^- anion which is thus formed causes the hydrolysis of the ester functions of DMAD to give methanol and the butynedioate dianion. The latter is isolated as the copper(II) complex.

Investigation of the the reaction of (1,2-naphthoquinone 1-oximato)lithium(I) with dimethyl

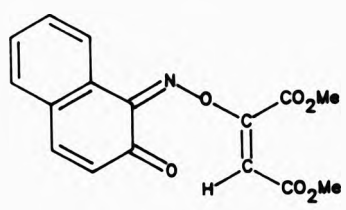


(4)


R
Cu
2
+
4
+
2 H2O
CO2Me
CO2Me
EGDE/H2O
OH
CO2Me
CO2Me
+
Cu2+
+
2OH−
OMe
OMe
Cu
2MeOH

Scheme 3.4

acetylenedicarboxylate showed that Michael addition occurs and products 5 and 6 result. In contrast the lithium complexes derived from 1,2-naphthoquinone 2-oxime [e.g. Li(2-nqo).1/2EtOH and Li(2-nqo)(2-nqoH)], give the cycloadduct (2, R = 7,8-(CH=CHCH=CH)) as well as the open chain addition product (7). The major metal containing product arising from the reactions is the lithium derivative of the hydrolysed adduct (e.g. 8).[10]



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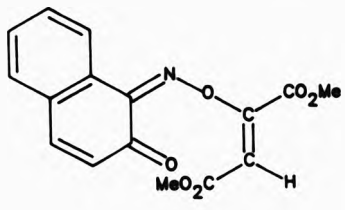

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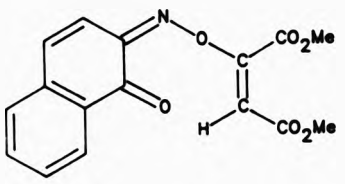

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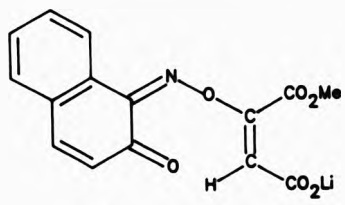
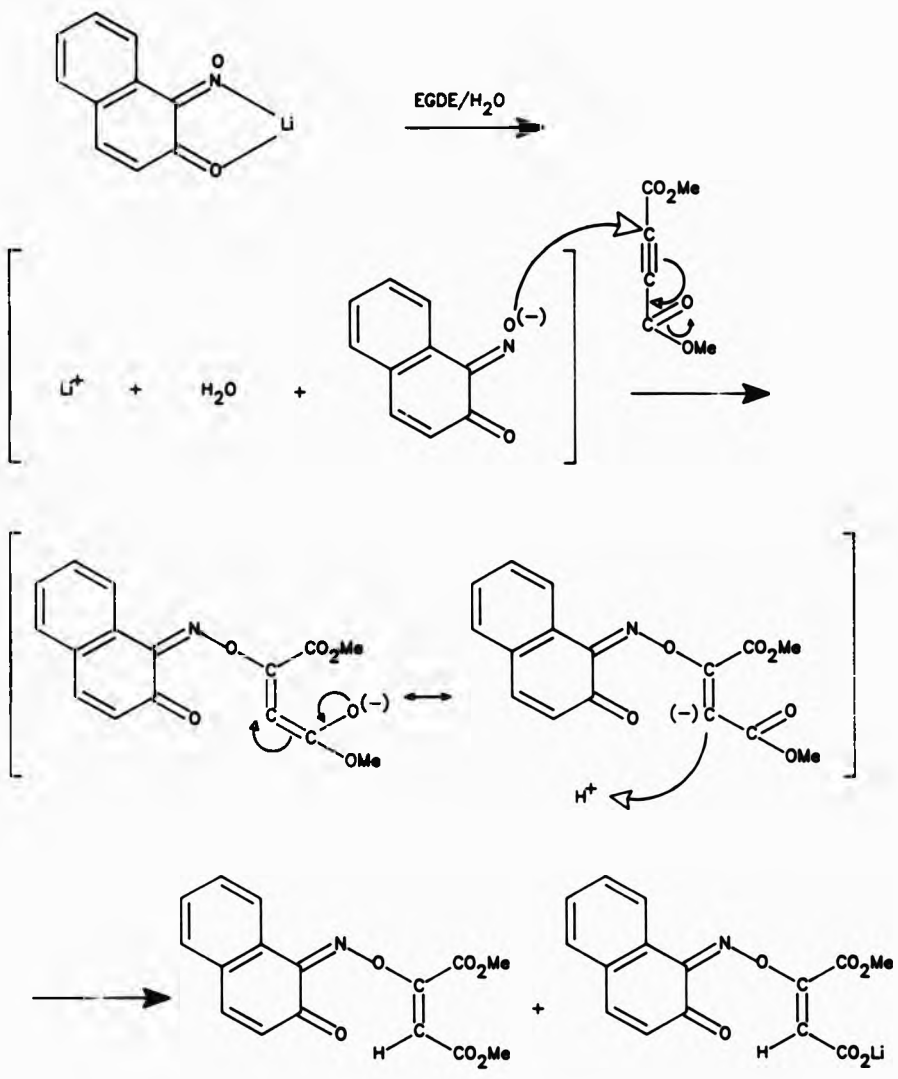


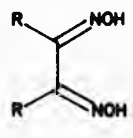
(8)

A mechanism suggested for the formation of the open chain adducts from the reaction of the lithium quinone oximic complexes with dimethyl acetylenedicarboxylate is presented in Scheme 3.5 .

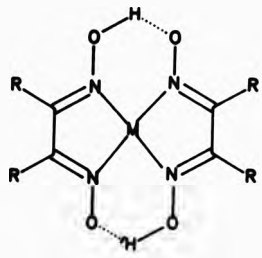


Scheme 3.5

Dioximes (9, R = NH_2, Ph) and their nickel(II) and copper(II) complexes have also been reported to react with dimethyl acetylenedicarboxylate under reflux conditions. In these cases 1,3-dipolar cycloaddition occurs to give a 2:1 isoxozalidine adduct (11).[13] The main metal containing product has been formulated as the hydrated metal(II) butynedioate. Michael addition or cycloaddition was suggested to occur either intermolecularly or intramolecularly, thus leading to formation of different types of 2:1 adducts. A mechanism has been suggested for the formation of the 2:1 adduct from the reactions of the metal(II) dioximic complexes and is outlined in Scheme 3.6 in an improved form.



(9)



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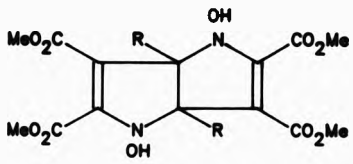

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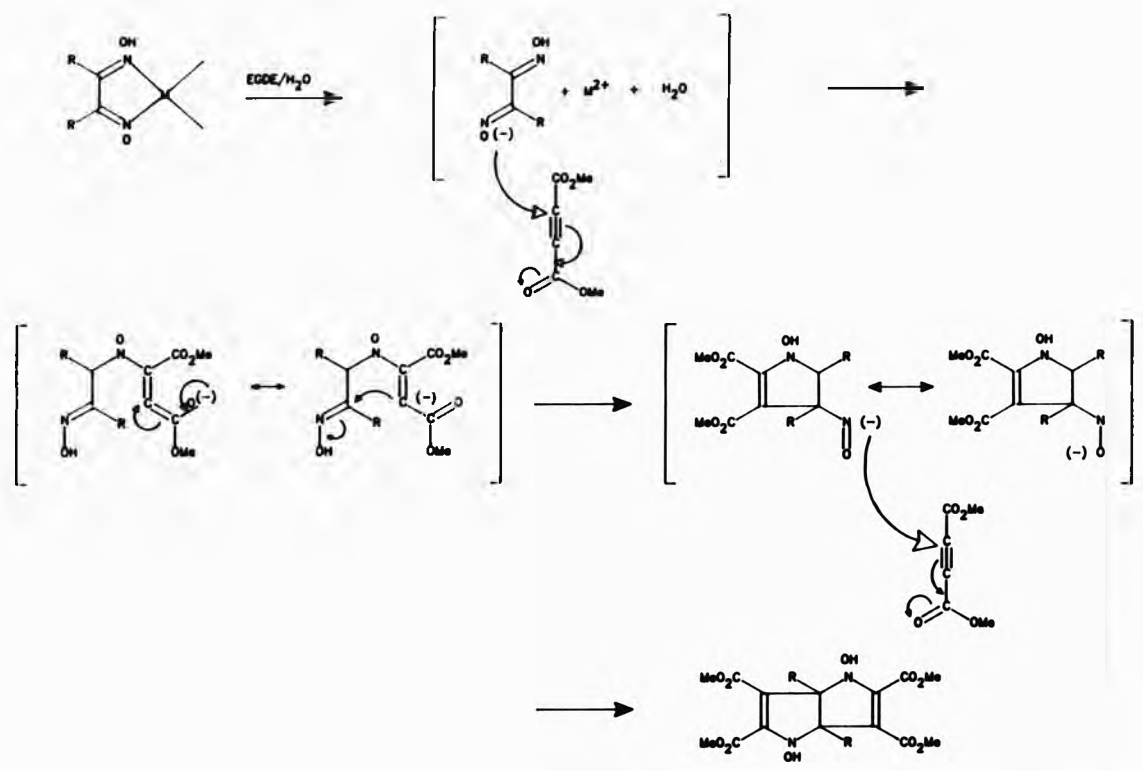


Scheme 3.6

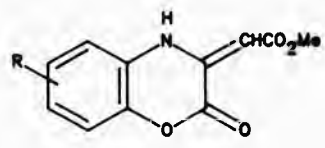
From the studies summarised above it can be concluded that in the reactions of metal(II) complexes of quinone mono-oximes with dimethyl acetylenedicarboxylate in aqueous ethylene glycol dimethyl ether, the metal, the type of the oximic ligand, and the reaction conditions have a pronounced effect on the nature of the organic products.

3.3 Present Studies of the Reaction of Metal Complexes of Quinone Mono-oximes Towards Dimethyl Acetylenedicarboxylate and Methyl Propiolate

During the present study the reactions of the nickel(II) complexes, $Ni(Rqo)_2$ [R = 4-Me, 4-Cl, 4-Br, 3,4-(CH=CHCH=CH), 5,6-(CH=CHCH=CH)] and of the new complex $Cu(5\text{-}Acqo)_2$ with dimethyl acetylenedicarboxylate were examined. The behaviour of some of these complexes [$M(1\text{-}nqo)_2$, $M(2\text{-}nqo)_2$ and $M(5\text{-}Acqo)_2$ (M = Ni, Cu)] with methyl propiolate, was also investigated. In addition the previously reported reactions of five copper(II) complexes [$Cu(Rqo)_2$ [R = 4-Me, 4-Cl, 4-Br, 3,4-(CH=CHCH=CH), 5,6-(CH=CHCH=CH)] and of $Co(1\text{-}nqo)_3$ with dimethyl acetylenedicarboxylate were reexamined.

In line with previous findings $Co(1\text{-}nqo)_3$ showed no reaction with dimethyl acetylenedicarboxylate.[8] In the case of reactions involving $M(Rqo)_2$/DMAD [M = Ni, Cu; R = 3,4- or 5,6-(CH=CHCH=CH)] it was found that both systems afford the 1,4-naphthoxazine cycloadducts but at

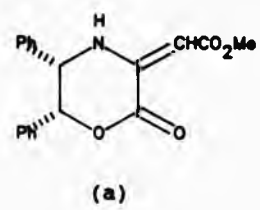
lower yields than reported previously.[8] In contrast in the case of the $M(Rqo)_2$/DMAD [M = Ni, Cu; R = 4-Me, 4-Br, 4-Cl] systems, the formation of another novel addition product was found to accompany the formation of the 1,4-oxazine cycloadduct. The new type of product was characterised as the 1,4-benzoxazinone (17). In the case of the $Ni(Rqo)_2$/DMAD systems, the yield of this product was found to be higher than that obtained from reactions involving the corresponding copper complexes. In particular in the case of the $Ni(4\text{-}Brqo)_2$/DMAD system the formation of the 1,4-benzoxazinone derivative was almost exclusively favoured to that of the 1,4-benzoxazine cycloadduct when the molar ratio of DMAD:complex exceeded four (Table 3.2).

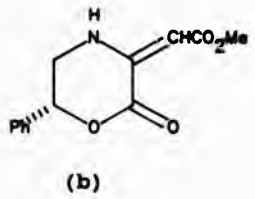


R = Br, Cl, Me

(17)

Recently related compounds (e.g. 12) have been obtained by the stereoselective alkylation of the enolate synthon N-acyl-2,3,5,6-tetrahydro-4H-oxazin-2-one bearing either 5-phenyl or 5,6-diphenyl substituents.[14,15] It has been reported that these compounds have chemotherapeutic properties.[16,17] Consequently an assessment of the





(a) (b)

(12)

chemotherapeutic properties of benzoxazinones (17), obtained during this study will be desirable.

All 1,4-oxazine and 1,4-oxazinone products arising from the above reactions were fully characterised by elemental analysis, m.s., i.r., and ^{1}H n.m.r. spectroscopy. In addition an X-ray crystallographic study of the 1,4-benzoxazinone derivative (17, R = Br) isolated from the $Ni(4\text{-}Brqo)_2$/DMAD system has been carried out during this study. These results are presented in the following sections of this chapter.

3.3.1 Reactions of Nickel(II) Complexes of Quinone Mono-oximes with Dimethyl Acetylenedicarboxylate

An earlier study of the system $Ni(4\text{-}Clqo)_2$/DMAD has led to the conclusion that DMAD reacts sluggishly with the nickel complex in aqueous EGDE to give the benzoxazine (2, R = 6-Cl) . Furthermore no reaction was observed in anhydrous methanol.[9]

During the present study the reaction of six nickel quinone oximato complexes with DMAD was undertaken. These reactions were carried out under various experimental conditions.

In general it has been established that whereas short reaction times, low temperatures or low DMAD:$Ni(qo)_2$ molar ratios lead to high recovery of the metal complex, complete conversion can be achieved by using higher DMAD:complex ratios in refluxing EGDE/H_2O for 24 hours (Table 3.2).

All systems investigated afforded an insoluble metal containing solid and a mixture of two organic products. In general the products arising from these reactions were separated using the procedure outlined in Scheme 3.7.

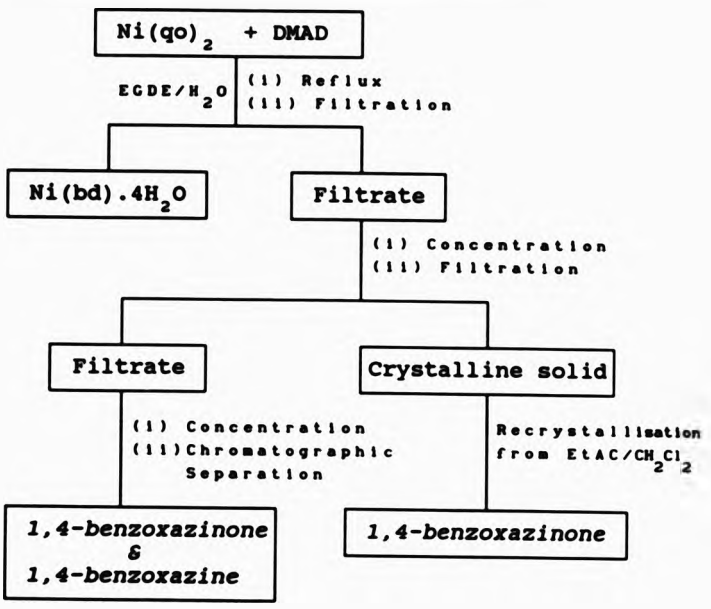
The Nature of the Metal Containing Products Obtained from $Ni(qo)_2$/DMAD Systems

Each of the $Ni(qo)_2$/DMAD systems investigated afforded a metal containing solid which was separated from the reaction mixture by filtration. These solids had very similar i.r. spectra (e.g. Fig. 3.1) and fairly similar elemental analysis. Small amounts of nitrogen found in these solids suggested the presence of nitrogen containing impurities which could not be removed by digesting the solids in refluxing methanol. However, in

Table 3.2 Summary of the Reactions of Nickel(II) Complexes of Quinone Mono-oximes (C) with Dimethyl Acetylenedicarboxylate (D)

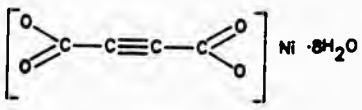
Metal Complex	Molar Ratios	Products		
	C : D	1,4-oxazine (%)	1,4-oxazine 2-one (%)	$Ni(bd).nH_2O$ (%)†
$Ni(1\text{-nqo})_2$	1 : 8	70	-	70
$Ni(2\text{-nqo})_2$	1 : 4	27	-	44
$Ni(4\text{-Meqo})_2$	1 : 4	65	20	66
$Ni(4\text{-Brqo})_2$	1 : 4	32	35	33
$Ni(4\text{-Brqo})_2$	1 : 5	-	88	42
$Ni(4\text{-Clqo})_2$	1 : 4	25	30	38
$Ni(5\text{-Acqo})_2$	1 : 4	68	-	71

† Based on nikel content



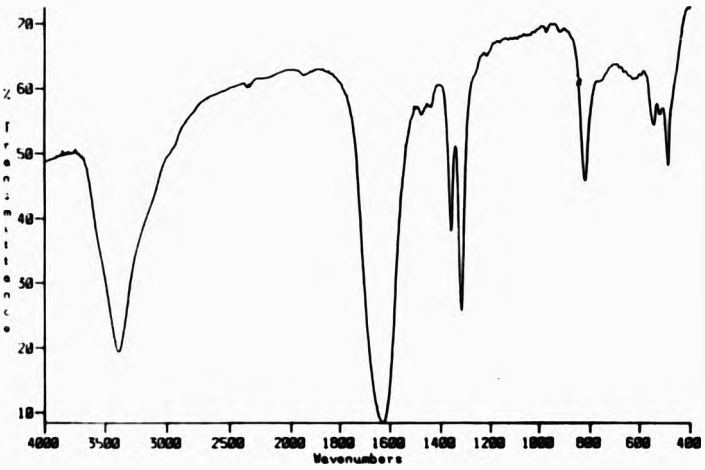
Scheme 3.7

some cases these impurities were removed by washing the solids with water. The elemental analysis of the solids which did not contain nitrogen impurities, indicated the presence of four carbons per metal, thus suggesting their formulation as the octahydrated nickel(II) butynedioate (13). The i.r. spectra of all solids



(13)

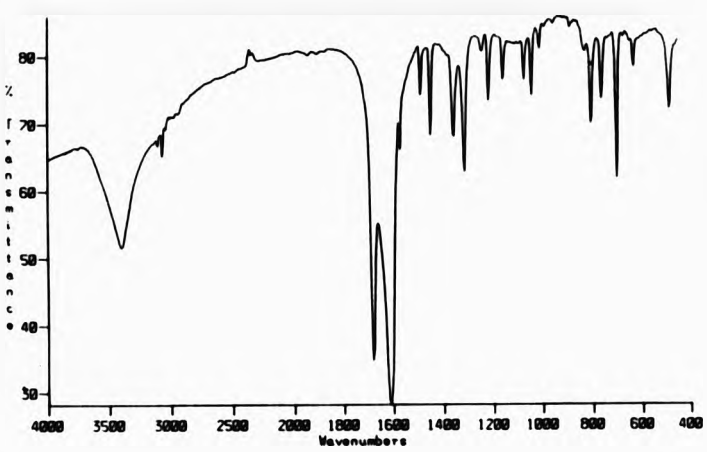
Fig 3.1 Infra-red Spectrum of Nickel(II) Butynedioate Octahydrate



contained bands at 3400, 1650-1630 and 1359 cm^{-1} assignable to the νOH and νCO. Their room temperature magnetic moments were found to be low *ca.* 2.00 μ_B. These values suggested association which is not unusual for metal carboxylates.[18]

In the case of the metal containing solids isolated from the systems involving $Ni(1\text{-nqo})_2$ and $Ni(2\text{-nqo})_2$ complexes, reaction with pyridine afforded solids whose elemental analysis is indicative of the formulation $Ni(bd)(py).nH_2O$ (n = 1, 2). These mono pyridine adducts had well defined i.r. spectra (e.g. Fig. 3.2) with absorptions at 3401, 1682 and 1606 cm^{-1} indicative of

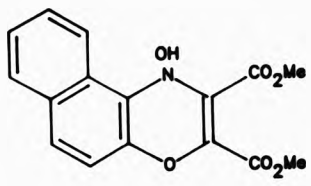
Fig 3.2 Infra-red Spectrum of Ni(bd)(py).nH$_2$O (n = 1, 2)



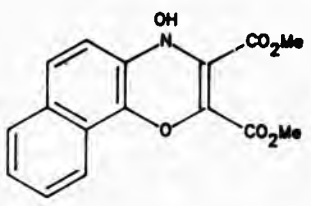
νOH and νCO respectively. The finger print region was in accord with the presence of pyridine.

The Nature of the Organic Products Isolated from Ni(qo)$_2$ /DMAD Systems

The organic products arising from the systems involving Ni(1-nqo)$_2$ and Ni(2-nqo)$_2$ were found to be the 1,4-naphthoxazine cycloadducts (14) and (15) respectively. This was indicated by melting point[8], m.s., i.r. and ^{1}H n.m.r. spectroscopy.

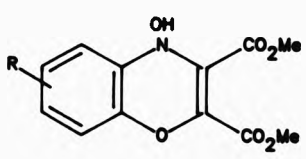


(14)

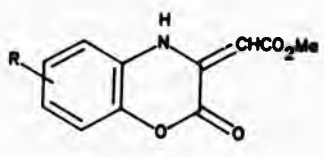


(15)

In the case of the Ni(4-Brqo)$_2$/DMAD, Ni(4-Clqo)$_2$/DMAD and Ni(4-Meqo)$_2$/DMAD systems two major organic products were isolated from each system. These products were found to be the 1,4-benzoxazine cycloadduct (16, R = 6-Br, 6-Cl, 6-Me) and another novel type of product which has not been reported previously. An X-ray crystallographic study of the latter product arising from the Ni(4-Brqo)$_2$/DMAD system has shown it to be the 1,4-benzoxazinone (17, where R = 6-Br). The corresponding products isolated from the other systems were fully characterised by elemental analysis, i.r., m.s., and ^{1}H n.m.r. spectroscopy. Previously,[10,13] only



(16)



(17)

R = Br, Cl, Me

limited spectroscopic data have been reported on the these derivatives. The results of infra-red, ^{1}H nuclear magnetic resonance and mass spectroscopic investigations carried out during this study are presented in the following section of this Chapter.

Spectroscopic Studies of the Organic Products Isolated from the Ni(qo)$_2$/DMAD Systems

The i.r. spectra of the 1,4-naphthoxazines (14) and (15), are very similar and include absorptions at *ca.* 3370, 1760, and 1720 cm^{-1} due to νOH of the hydroxy and νCO of the ester carbonyl groups (Table 3.3). A typical spectrum is presented in Fig. 3.3. The ^{1}H n.m.r. spectra (e.g. Fig. 3.4, Table 3.4) of the naphthoxazines (14) and (15) exhibit resonances at *ca.* 3.90 and 4.00 ppm (singlets) due to six carbomethoxy protons, at *ca.* 7.00 ppm (singlet) due to the proton of the hydroxy group and at *ca.* 7.27 - 8.63 ppm (multiplets) due to the six aromatic protons. In the case of naphthoxazine 14 (Fig. 3.4), the third proton is coupled to the second and fourth protons and hence should give rise to a doublet of doublets. However, in the spectrum there are only three lines due to this proton. This may be explained by the overlap of the two centre lines. Similar explanation is also valid for the fourth proton. In the case of 1,4-naphthoxazine (15) the spectrum is complex (second order) and assignments can not be made. The mass spectra (e.g. Fig 3.5) of both compounds showed

Fig. 3.3 Infra-red Spectrum of 4-Hydroxy-2,3-dimethoxycarbonyl-1,4-naphthoxazine (14)

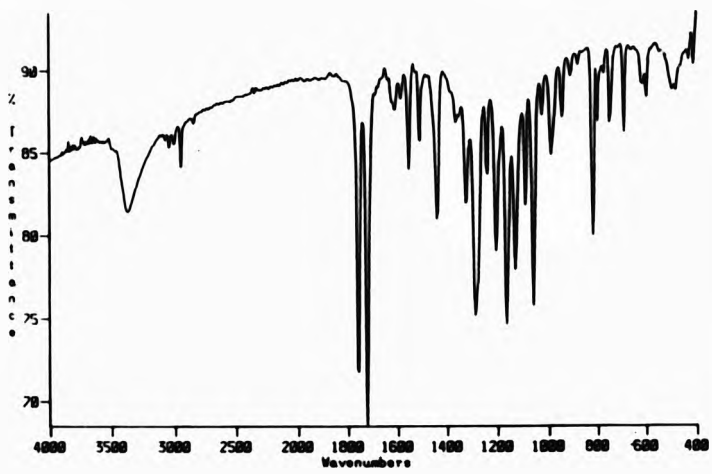


Table 3.3 νOH and νCO Absorptions (cm^{-1}) of 1,4-Oxazine Derivatives

1,4-Oxazine	νOH	νCO[a]	νCO[a]
14	3372	1760	1723
15	3422	1775	1719
16, R = 6-Br	3275	1770	1727
16, R = 6-Cl	3240	1770	1728
16, R = 6-Me	3239	1767	1724

a, b=Ester carbonyl absorption frequencies

Fig. 3.4 ^1H Nuclear Magnetic Resonance Spectrum of 4-Hydroxy-2,3-dimethoxylcarbonyl-1,4-naphthoxazine (14) in $CDCl_3$

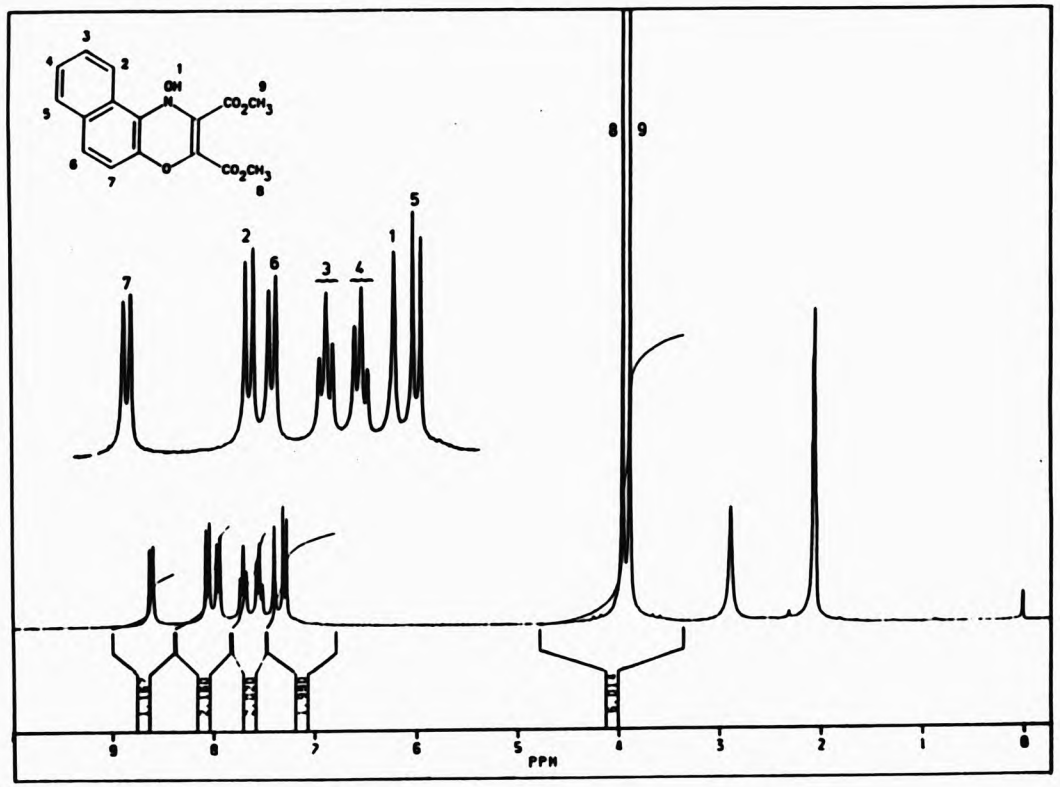


Table 3.4 ^{1}H Nuclear Magnetic Resonance Spectral Assignments For the 1,4-Oxazine Derivatives

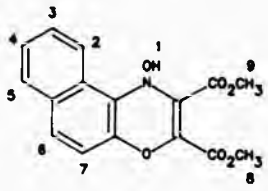
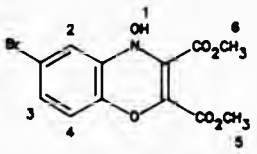
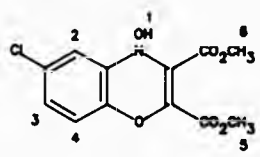
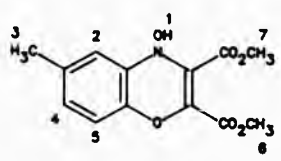
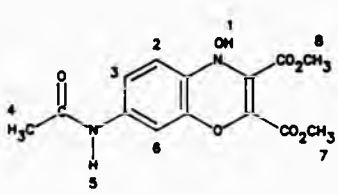
Compound	Assignment	Multiplicity (J/Hz)	δ/ppm
	1	s	7.39
	2	d ($J_{2,3}$ = 8.92)	8.05
	3	m	7.70
	4	m	7.54
	5	d ($J_{4,5}$ = 8.93)	7.29
	6	d ($J_{6,7}$ = 8.06)	7.95
	7	d ($J_{7,6}$ = 8.33)	8.61
	8	s	3.95
	9	s	3.88
	1	s	7.50
	2	d ($J_{2,3}$ = 2.43)	7.78
	3	dd ($J_{2,3}$ & $J_{4,5}$)	7.62
	4	d ($J_{3,4}$ = 8.62)	7.08
	5	s	3.90
	6	s	3.85
	1	s	8.98
	2	d ($J_{2,3}$ = 2.56)	7.75
	3	dd ($J_{2,3}$ & $J_{3,4}$)	7.52
	4	d ($J_{3,4}$ = 7.88)	7.22
	5	s	3.92
	6	s	3.86

Table 3.4 cont.

Compound	Assignment	Multiplicity (J/HZ)	δ/PPM
	1	s	5.11
	2	d ($J_{2,4}$ = 1.35)	7.50
	3	dd ($J_{2,4}$ & $J_{4,5}$)	7.20
	4	d ($J_{4,5}$ = 8.29)	6.92
	5	s	3.93
	6	s	3.96
	7	s	2.35
	1	s	8.67
	2	d ($J_{2,3}$ = 8.66)	7.54
	3	dd ($J_{2,3}$ & $J_{3,6}$)	7.26
	4	s	2.08
	5	s	10.23
	6	d ($J_{3,6}$ = 5.67)	7.26
	7	s	3.81
	8	s	3.76

d=Doublet; dd=Doublet of doublets; s=Singlet
m=Multiplet

Fig. 3.5 Electron Impact Mass Spectrum of 4-Hydroxy-2,3-dimethoxycarbonyl-1,4-naphthoxazine (14)

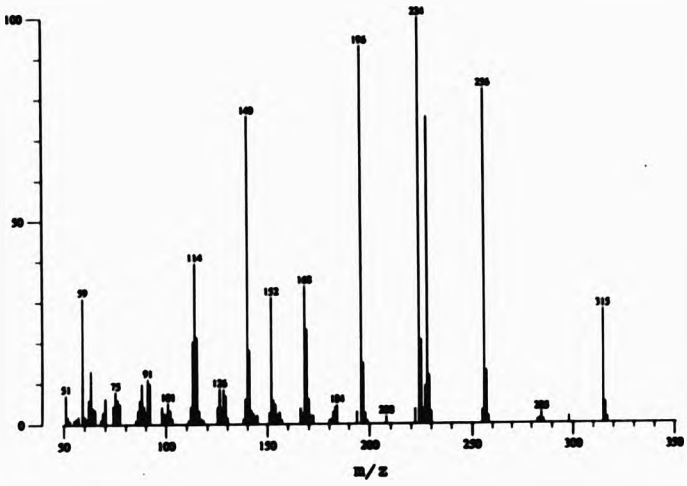


Table 3.5 Relative Aboundances of Ions in the Mass Spectrum of 4-Hydroxy-2,3-dimethoxycarbonyl-1,4-naphthoxazine (14)

Ion Assignment	Intensity	m/z
$[M]^{+\cdot}$	28	315
$[M - NO]^{+\cdot}$	3	285
$[M - MeCO_2^{\cdot}]^{+}$	82	256
$[M - (MeCO_2^{\cdot} + MeOH)]^{+}$	100	224
$[M - (MeCO_2^{\cdot} + MeOH + CO)]^{+}$	93	196
$[M - (MeOH + MeCO_2^{\cdot} + 2CO)]^{+}$	34	168

intense molecular ion peaks at 315 and exhibit fragmentation patterns supporting the formulations (Table 3.5).

The i.r. spectra of the 1,4-benzoxazines (16, R = 6-Br, 6-Cl, 6-Me) indicate the presence of hydroxy and ester carbonyl groups (Table 3.3). In their ^{1}H n.m.r. spectra (e.g. Fig 3.6) the six methyl protons of the ester groups appear at *ca.* 3.80 and 3.90 ppm as two singlets, the proton of the hydroxy group at *ca.* 7.00 ppm as a singlet and the three aromatic protons at *ca.* 7.06 - 7.78 ppm as a multiplet (Table 3.4). The mass spectra (e.g. Fig 3.7) of all compounds show fairly intense molecular ion peaks and exhibit fragmentation patterns involving loss of groups such as $OH^{\bullet}$, $CHO^{\bullet}$, and $MeCO_2^{\bullet}$ (Table 3.6).

Fig. 3.6 ^{1}H Nuclear Magnetic Resonance Spectrum of 6-Bromo-4-hdroxy-2.3-dimethoxycarbonyl -1.4-benzoxazine (16. R = 6-Br) in d_6-DMSO

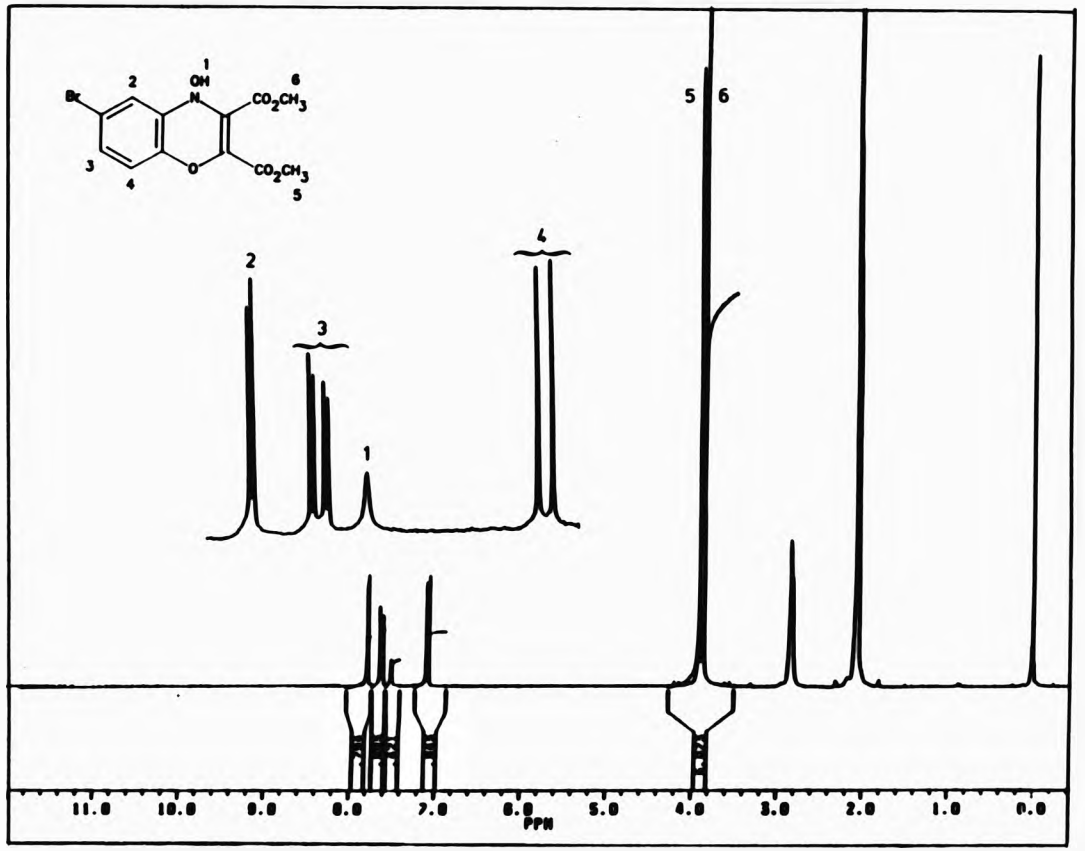


Fig 3.7 Electron Impact Mass Spectrum of 6-Bromo-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine (16, R = 6-Br)

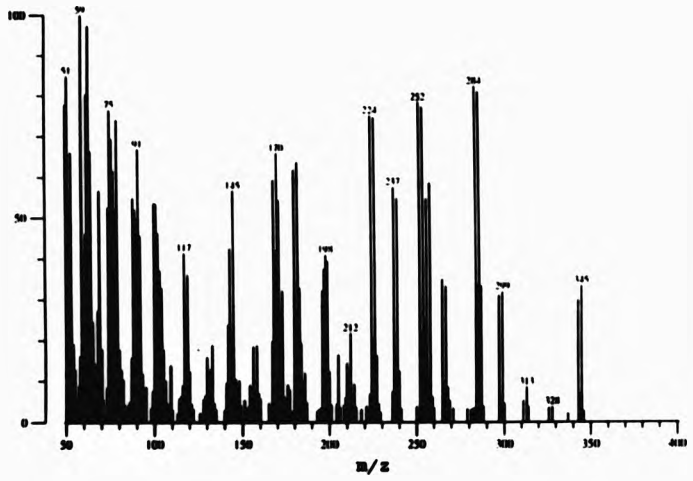


Table 3.6 Relative Abundances of Ions in the Mass Spectrum of 6-Bromo-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine (16, R = 6-Br)

Ion Assignment	Relative Abundance (%)	m/z
$[M]^{+\cdot}$	28	343
$[M - OH^{\cdot}]^{+}$	3	326
$[M - (CHO + OH)]^{+\cdot}$	31	297
$[M - MeCO_2^{\cdot}]^{+}$	82	284
$[M - (MeCO_2^{\cdot} + MeOH)]^{+}$	78	252
$[M - (MeOH + CO + MeCO_2^{\cdot})]^{+}$	75	224

The i.r. spectra (e.g. Fig. 3.8) of the 1,4-benzoxazinones (17, R = 6-Br, 6-Cl, 6-Me) include absorptions at *ca.* 3400, 1770, 1640 cm^{-1} assignable to νNH of the imine and νCO of the ester carbonyl and the lactone groups (Table 3.7). Their ^{1}H n.m.r. spectra (e.g. Fig. 3.9) show the expected resonances due to carbomethoxy vinylic and aromatic protons. A singlet at 10.60 ppm also indicates the presence of an exchangeable proton due to the imino group (Table 3.8). In their mass spectra (e.g. Fig. 3.10) the parent ions correspond to the base peaks. Prominent peaks due to the loss of MeOH, CO and HCN from the parent ion are also present (Table 3.9).

Fig. 3.8 Infra-red Spectrum of 6-Bromo-3.4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1.4-benzoxazin-2-one (17. R = 6-Br)

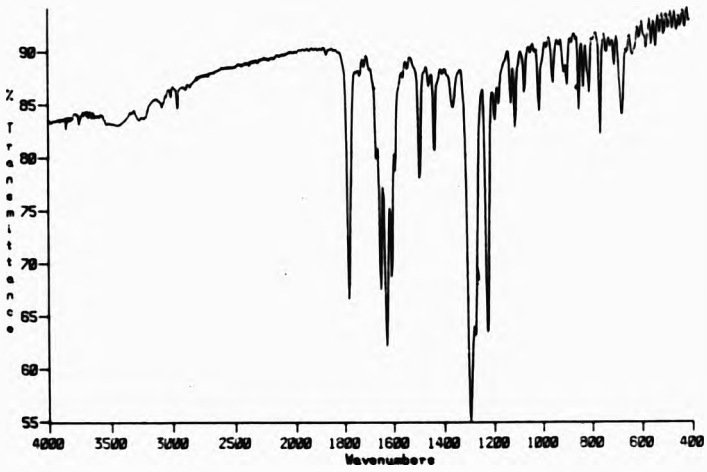


Table 3.7 νNH and νCO Absorptions (cm^{-1}) of 1.4-Oxazin-2-one Derivatives

1,4-Oxazin-2-one	νNH	νCO[a]	νCO[b]
17, R = Br	3425	1781	1651
17, R = Cl	3369	1771	1630
17, R = Me	3441	1758	1656

a=Ester carbonyl absorption frequencies
b=Lactone absorption frequencies

Fig. 3.9 ^{1}H Nuclear Magnetic Resonance Spectrum of 6-Bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one (17, R = 6-Br) in $CDCl_3$

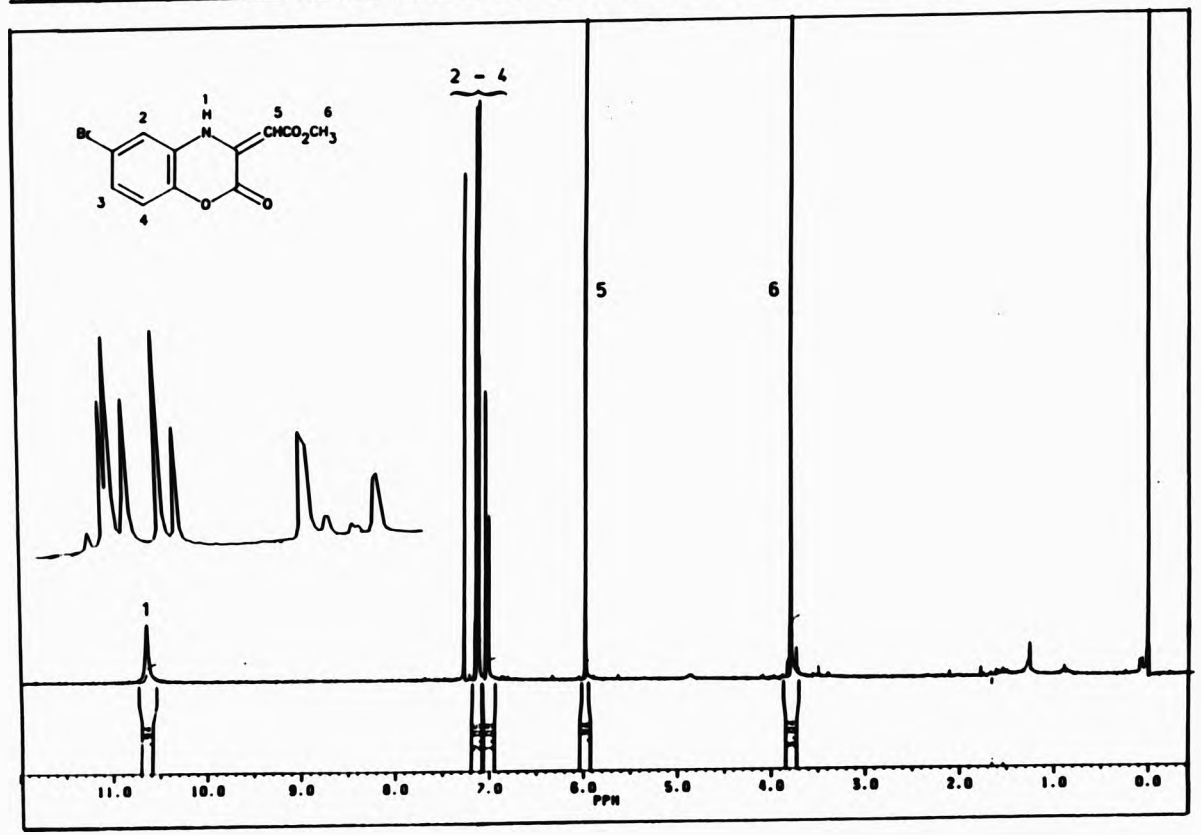
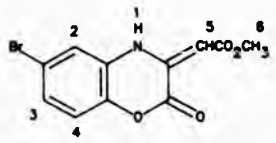
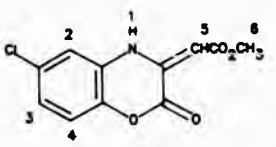
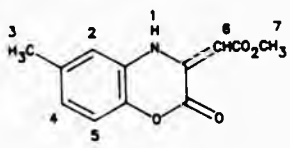


Table 3.8 ^{1}H Nuclear Magnetic Resonances Spectoral Assignments for 1,4-Benzoxazin-2-one Derivatives

Compound	Assignment	Mutipilicity	δ/ppm
	1	s	10.65
	2, 3, 4*	m	7.00 - 7.26
	5	s	5.78
	6	s	3.78
	1	s	10.66
	2, 3, 4*	m	6.96 - 7.26
	5	s	5.98
	6	s	3.78
	1	s	10.61
	2, 3, 4*	m	6.78 - 7.26
	5	s	2.33
	6	s	5.92
	7	s	3.78

s=Singlet; m=Multiplet; *=Second order

Fig. 3.10 Electron Impact Mass Spectrum of 6-Bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one (17, R = 6-Br)

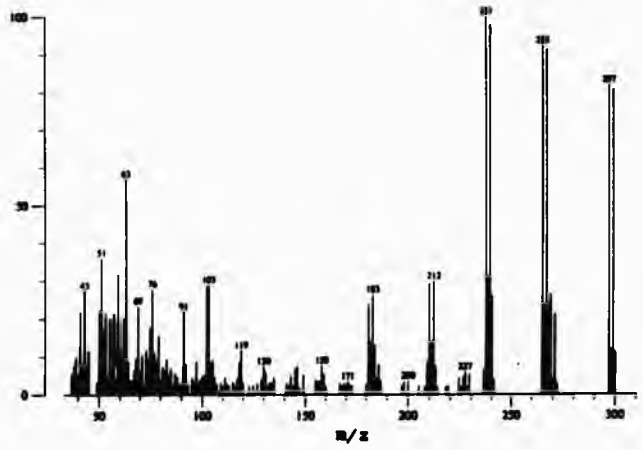


Table 3.9 Relative Abundances of Ions in the Mass Spectrum of 6-Bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one (17, R = 6-Br)

Ion Assignment	Relative Aboundance (%)	m/z
$[M]^{+\cdot}$	65	297
$[M - MeOH]^{+\cdot}$	93	265
$[M - (MeOH + CO)]^{+\cdot}$	100	237
$[M - (MeOH + CO + HCN)]^{+\cdot}$	30	210
$[M - (MeCO_2^{\cdot} + HCN + CHO^{\cdot}]^{+}$	30	181

3.3.2 Reactions of Copper(II) Complexes of Quinone Mono-oximes with Dimethyl Acetylenedicarboxylate

As noted earlier in the first study[8] of the reaction of copper(II) quinone oximic complexes with dimethyl acetylenedicarboxylate, the behaviour of seven complexes (Table 3.1) with the dienophile was examined. It was reported that in all cases the reactions lead to the formation of an oxazine in high yield and of a metal containing solid which was not identified.

Subsequently, further studies of the systems $Cu(1\text{-nqo})_2$/DMAD and $Cu(2\text{-nqo})_2$/DMAD led to the conclusion that both systems afford the same metal containing solid.[9] Although the analytical data were not fully satisfactory, the solid was formulated as copper(II) butynedioate. The yield of the naphthoxazine arising from the system involving $Cu(1\text{-nqo})_2$/DMAD was found to be comparable to that reported in the first study. However the yield of the naphthoxazine obtained from the $Cu(2\text{-nqo})_2$/DMAD system was found to be much lower than reported initially.

During this work, most of the systems $Cu(qo)_2$/DMAD systems reported in the first study were reexamined. In addition the reaction of bis(5-acetylamino 1,2-benzoquinone 2-oximato)copper(II) with dimethyl acetylenedicarboxylate was investigated. The systems examined are summarised in Table 3.10.

Table 3.10 Summary of the Reactions Copper of Complexes of Quinone Mono-oximes (C) with Dimethyl Acetylenedicarboxylate (D) Investigated during the Present Study

Metal Complex	Molar Ratios	Products		
	C : D	1,4-Oxazine (%)	1,4-Oxazinone (%)	Cu(bd).nH O_2 (%)†
$Cu(1\text{-nqo})_2$	1 : 4	70	-	90
$Cu(2\text{-nqo})_2$	1 : 4	38	-	92
$Cu(4\text{-Brqo})_2$	1 : 4	54	11	87
$Cu(4\text{-Clqo})_2$	1 : 4	32	27	62
$Cu(4\text{-Meqo})_2$	1 : 4	75	1.4	67
$Cu(5\text{-Acqo})_2$	1 : 4	76	-	88

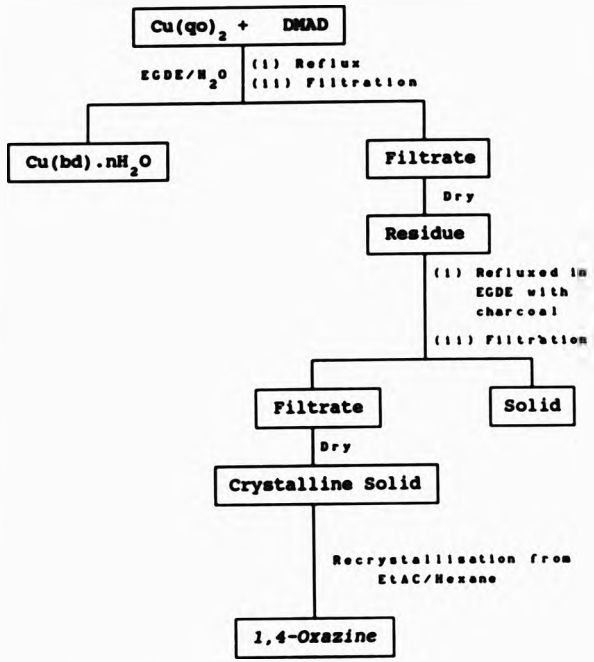
†=Based on copper content

The specific aims of this work were to (a) fully characterise all the products arising from the reactions, (b) identify the factors leading to their formation, (c) investigate the mechanism of the reactions.

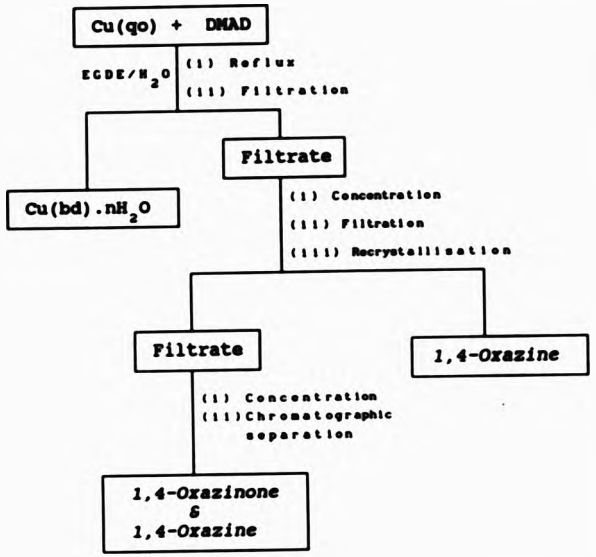
In the present study in addition to the separation technique employed by the previous workers (Scheme 3.8)[8,10] another technique (Scheme 3.9) involving chromatographic separation was used. In general irrespective of the separation technique used, the yield of the phenoxazine was found to be lower than reported previously.[8]

The Nature of the Metal Containing Solid Arising from Cu(qo)$_2$/DMAD Systems

Each of the Cu(qo)$_2$/DMAD systems investigated afforded a metal containing solid. The i.r. spectra of all the solids were found to be simple and similar to those of the hydrated nickel(II) butynedioate species (discussed in section 3.3.1). However, small amounts of nitrogen containing impurities found in these solids could be neither removed by digestion in refluxing methanol nor by washing with water. The elemental analysis for these products indicated the presence of three carbons per metal. On this basis the solids are formulated as crude copper(II) butynedioate. The solid obtained from the Cu(4-Clqo)$_2$/DMAD system was stirred with pyridine. This



Scheme 3.8



Scheme 3.9

led to a product whose i.r. spectrum was well defined. The spectrum showed bands at 3500 and 1600 - 1700 cm^{-1} assignable to νOH and νCO. Absorptions in the finger print region were indicative of pyridine. The elemental analysis indicated the presence of eight carbons per metal, suggesting the addition of a pyridine to each metal. However, no meaningful overall formulation could be deduced.

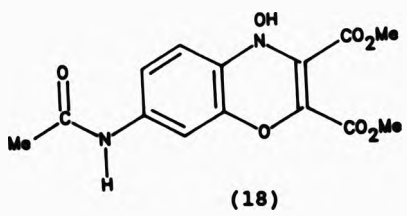
The Nature of the Organic Products Isolated from Cu(qo)$_2$/DMAD Systems

In the case of the Cu(1-nqo)/DMAD and Cu(2-nqo)$_2$/DMAD systems, the only organic products isolated by column chromatography were the 1,4-naphthoxazines (14) and (15).

As in the case of the Ni(Rqo)$_2$/DMAD (R = 4-Br, 4-Cl, 4-Me) systems the corresponding Cu(Rqo)$_2$/DMAD systems afforded the 1,4-benzoxazinone (17) in addition to the 1,4-benzoxazine (16). However the yields of these products vary considerably with the nature of the the ligand and the metal centre (Table 3.10).

Bis(5-acetylamino-1,2-benzoquinone 2-oximato)copper(II) reacted with dimethyl acetylenedicarboxylate in aqueous EGDE solution, to give *7-acetylamino-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine* (18) as the major product. Smaller amounts of a red organic product were

also isolated. On the basis of its elemental analysis the latter has been formulated as $C_{12}H_{14}NO_6$ but no further characterisation was possible.



(18)

Spectroscopic Studies of the Organic Products Isolated from the Cu(5-Acqo)$_2$/DMAD System.

The i.r. spectrum of the 1,4-benzoxazine (18) showed absorptions at 3557 and 3319 cm^{-1} due to the νOH and νNH respectively. Three intense absorption bands were also observed at 1764, 1732, and 1675 cm^{-1} assignable to the νCO of the amide and the two ester groups respectively. The ^{1}H n.m.r. (Fig. 3.11) showed the expected resonances at 2.06, 3.80, and 3.85 ppm due to nine methyl groups and at 7.31 - 7.60 ppm due to three aromatic protons. The presence of two exchangeable protons assignable to NH and OH protons was observed at 8.7 and 10.4 ppm (Table 3.4). In the mass spectrum (Fig. 3.12) there was a prominent parent ion peak at 321.9 and fragments arising from the loss of MeO$^{\cdot}$, MeCO$^{\cdot}$, OH$^{\cdot}$, and Ac$^{\cdot}$ from the parent ion (Table 3.11).

Fig. 3.11 ^1H Nuclear Magnetic Resonance Spectrum of 7-Acetylamino-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine (18) in d_6-DMSO

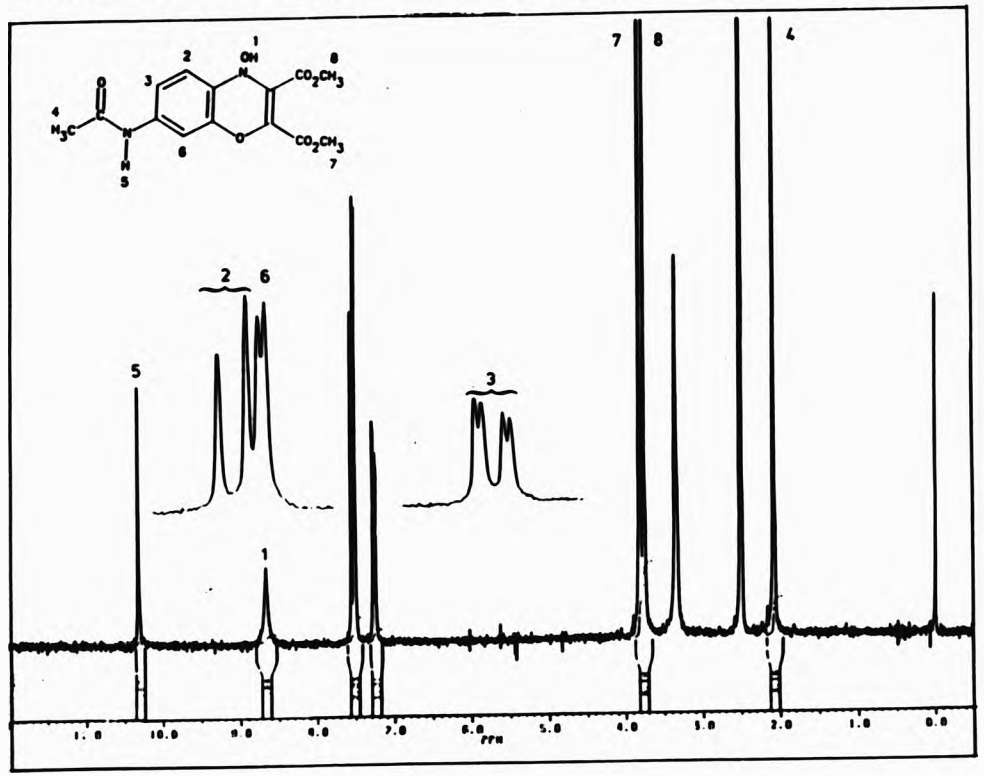


Fig. 3.12 Electron Impact Mass Spectrum of 7-Acetylamino-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine (18)

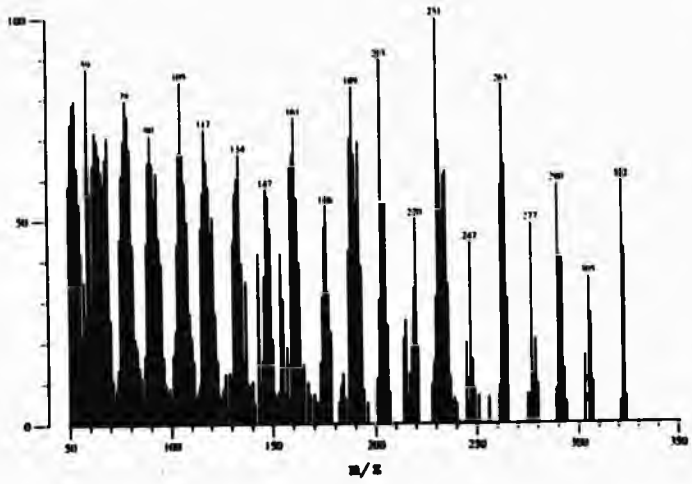


Table 3.11 Relative Abondances of Ions in the Mass Spectrum of 7-Acetylamino-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine (18)

Ion Assignment	Relative Aboundance (%)	m/z
$[M]^{+\cdot}$	59	322
$[M - OH^{\cdot}]^{+}$	36	305
$[M - (CO + OH^{\cdot})]^{+}$	49	277
$[M - MeCO_2^{\cdot}]^{+}$	83	263
$[M - MeCONH^{\cdot}]^{+}$	67	264
$[M - (MeOH + MeCO^{\cdot})]^{+}$	44	247
$[M - (MeOH + MeCO_2^{\cdot})]^{+}$	100	231
$[M - (Me^{\cdot} + CO + Me_2CO^{\cdot})]^{+}$	50	220
$[M - (MeOH + MeCO_2^{\cdot} + CO)]^{+}$	90	203

3.3.3 Studies of the Reaction of $M(qo)_2$ with Methyl Propiolate

During this work the reactions of $M(Rqo)_2$ [R = 5,6-(CH=CHCH=CH), 5-Ac and M = Ni, Cu) with methyl propiolate were also investigated. Previously no studies involving methyl propiolate have been reported.

The reaction of $Cu(1\text{-}nqo)_2$ with methyl propiolate was investigated under several different conditions (Table 3.12). It was found that when the reaction is carried out in aqueous EGDE under reflux for up to 6 h, 60% of the metal complex is recovered unchanged and some yellow organic product is formed. However, when a 18 h reflux time was used, all the metal complex reacted to give a metal containing solid, a major yellow organic product and a small amount of a red organic product. In contrast, the complexes $Ni(1\text{-}nqo)_2$, $Ni(5\text{-}Acqo)_2$, and $Cu(5\text{-}Acqo)_2$ (Table 3.12) showed little or no tendency to react with methyl propiolate even when an excess of the dienophile and long reflux periods were used. The complex $Ni(1\text{-}nqo)_2$ afforded the same yellow organic product as $Cu(1\text{-}nqo)_2$. However, the system involving $Cu(5\text{-}Acqo)_2$ gave a complex mixture of products which was not investigated.

The metal containing product isolated from $Cu(1\text{-}nqo)_2$/MP system had a simple well defined i.r. spectrum (Fig. 3.13). This resembled that of methyl propiolate

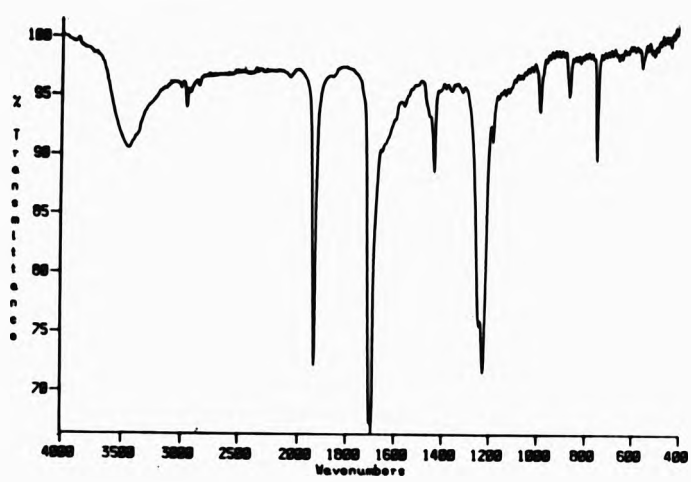
Table 3.12 Summary of the Reactions of Complexes of Quinone Mono-oximes with Methyl Propiolate (D)

Complex	Molar Ratio C : D	Reflux Time (h)	Complex [% Recovery]	Products A (%)††	B (%)	C (g)
$Cu(1\text{-nqo})_2$	1 : 4	3	65	-	27	-
$Cu(1\text{-nqo})_2$	1 : 4	6	54	-	31	-
$Cu(1\text{-nqo})_2$	1 : 4	18	-	77	65	0.13*
$Cu(5\text{-Acqo})_2$	1 : 4	18	73	-	-	0.16†
$Ni(1\text{-nqo})_2$	1 : 4	18	64	-	21	-
$Ni(1\text{-nqo})_2$	1 : 8	72	54	-	29	-
$Ni(5\text{-Acqo})_2$	1 : 4	18	95	-	-	-

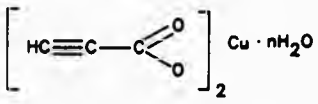
A=Hydrate metal(II)propynoate; B=1,4-Naphthoxazine (20/21); C=Other organics;

*=1,4-naphthoxazole (22); †=Mixture not investigated; ††=Based on copper content

Fig 3.13 Infra-red Spectrum of Hydrated Copper(II) Propynoate (19)

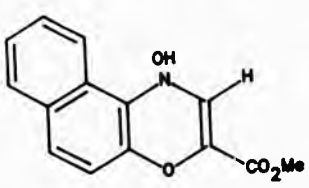


and included absorptions at 3448, 1931 and 1697 cm^{-1} indicating the presence of hydroxy, acetylenic and carboxylate groups. Its elemental analysis indicated the presence of six carbon atoms per copper, and suggested its formulation as the hydrated copper(II) propynoate, $Cu(pna)_2 . nH_2O$ (19).

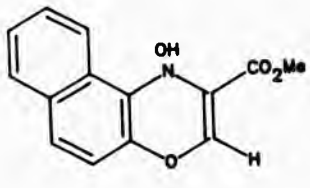


(19)

The elemental analysis and mass spectrum (Fig. 3.14) of the the yellow organic product obtained from the Cu(1-nqo)$_2$/MP and Ni(1-nqo)$_2$/MP systems suggested that it is either a Diels-Alder cycloadduct (20, 21), or an open chain Michael addition product (5, 6). The ^{1}H n.m.r. spectrum (Fig. 3.15) shows the presence of one vinylic hydrogen as expected for the cycloadduct formulation whilst the open chain formulation is precluded by the absence of two vinylic hydrogens. The other features of the spectrum [resonances due to the carbomethoxy protons, an exchangeable proton and a multiplet due to six aromatic protons] (Table 3.14) are also in accord with the cycloadduct formation but do not distinguish between structures 20 and 21. The i.r. spectrum (Fig. 3.16) is in accord with the cycloadduct formulation but again does not provide a means for distinguishing between the two possible structures.



(20)



(21)

Fig 3.14 Electron Impact Mass Spectrum of 4-Hydroxy-mono-methoxycarbonyl-1,4-naphthoxazine (20/21)

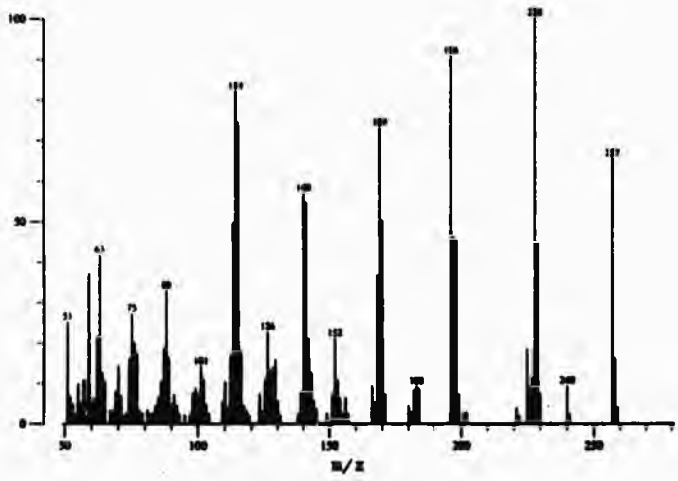


Table 3.13 Relative Aboundances of Ions in the Mass Spectrum of 4-Hydroxy-mono-methoxycarbonyl-1,4-naphthoxazine (20/21)

Ion Assignment	Relative Aboundance (%)	m/z
$[M]^{+\cdot}$	66	257
$[M - OH^{\cdot}]^{+}$	10	240
$[M - CHO^{\cdot}]^{+}$	100	228
$[M - (MeOH + CHO^{\cdot})]^{+}$	91	196
$[M - (MeCO_2H + CO)]^{+}$	73	169

Fig. 3.15 ^{1}H Nuclear Magnetic Resonance Spectrum of 4-Hydroxy-monomethoxycarbonyl-1,4-naphthoxazine (20)* in $CDCl_3$

*Although 4-Hydroxy-monomethoxycarbonyl-1,4-naphthoxazine (20) is shown the n.m.r. data are also compatible for its isomer (21) (see text page 146).

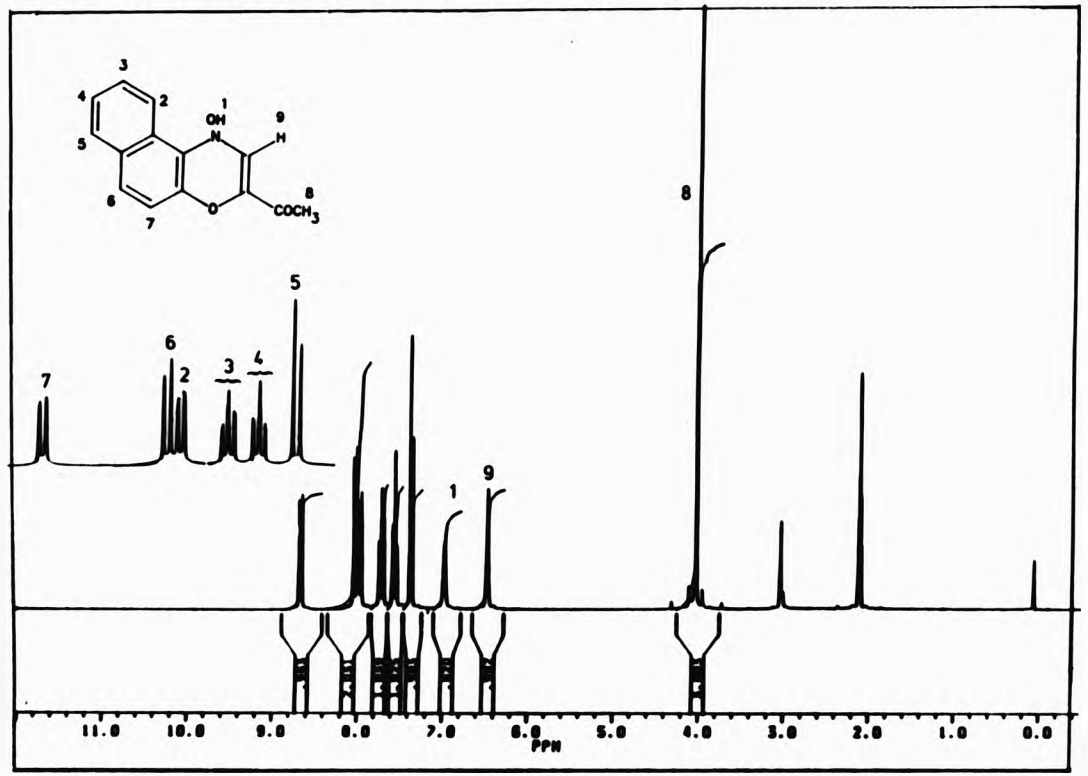
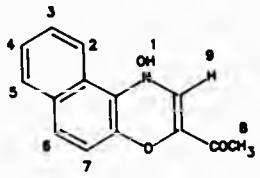
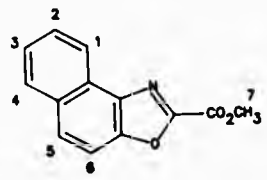
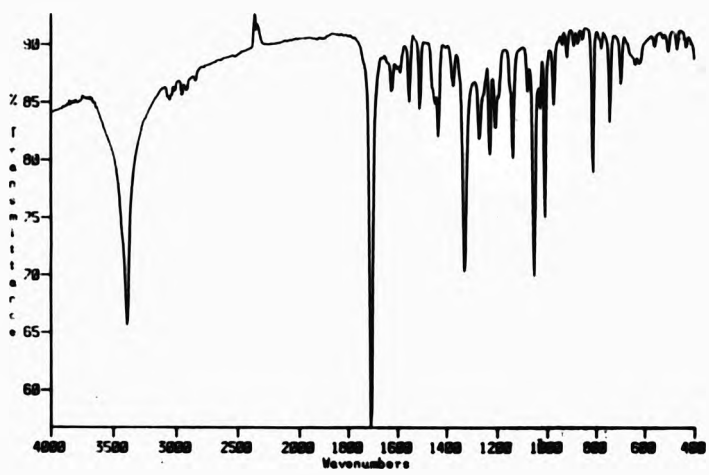


Table 3.14 Nuclear Magnetic Resonance Spectral Assignments for 1,4-Naphthoxazine (20)* and 1,4-Naphthoxazole (22)

Compound	Assignment	Multiplicity (J/Hz)	δ/ppm
	1	s	6.92
	2	d ($J_{2,3}$ = 8.88)	7.96
	3	m	7.67
	4	m	7.50
	5	d ($J_{4,5}$ = 8.90)	7.32
	6	d ($J_{6,7}$ = 7.94)	7.91
	7	d ($J_{7,6}$ = 8.53)	8.61
	8	s	4.05
	9	s	6.41
	1	d ($J_{1,2}$ = 10)	8.14
	2	m	7.80
	3	m	7.68
	4	d ($J_{4,3}$ = 9.10)	7.92
	5	d ($J_{5,6}$ = 10.0)	8.14
	6	d ($J_{5,6}$ = 9.36)	8.52
	7	s	4.08

d=Doublet; dd=Doublet of doublets; s=Singlet
*=Although 1,4-naphthoxazine (20) is shown, the n.m.r. data are also compatible with 1,4-naphthoxazine (21) (see text page 146)

Fig. 3.16 Infra-red Spectrum of 4-Hydroxy-mono-methoxycarbonyl-1,4-naphthoxazine (20/21)



The red product which was isolated from the Cu(1-nqo)$_2$/MP system has been characterised as 1,3-naphthoxazole-2-carboxylate (22) on the basis of its ^{1}H n.m.r., i.r. and mass spectra. The ^{1}H n.m.r. spectrum (Fig. 3.17, Table 3.14) shows the expected resonances due to six aromatic and three methyl protons of the carbomethoxy group and the i.r. spectrum (Fig. 3.18) includes an intense absorption due to νCO. An intense molecular ion peak and fragments arising by the loss of MeO$^{\cdot}$, CO_2 and $MeCO_2^{\cdot}$ are evident in the mass spectrum (Fig. 3.19, Table 3.15).

Fig. 3.18 ^1H Nuclear Magnetic Resonance Spectrum of 1,3-Naphthoxazol-2-carboxylate (22) in $CDCl_3$

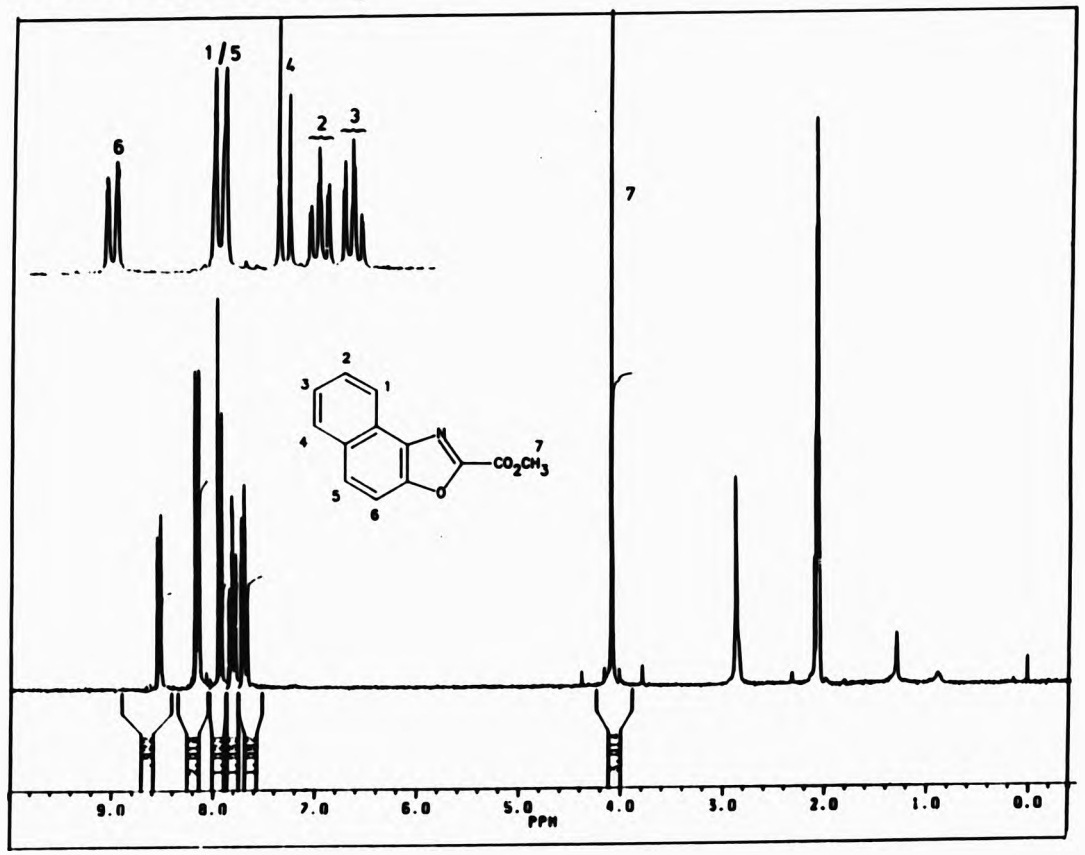


Fig. 3.18 Infra-red Spectrum of 1,3-Naphthoxazole-2-carboxylate (22)

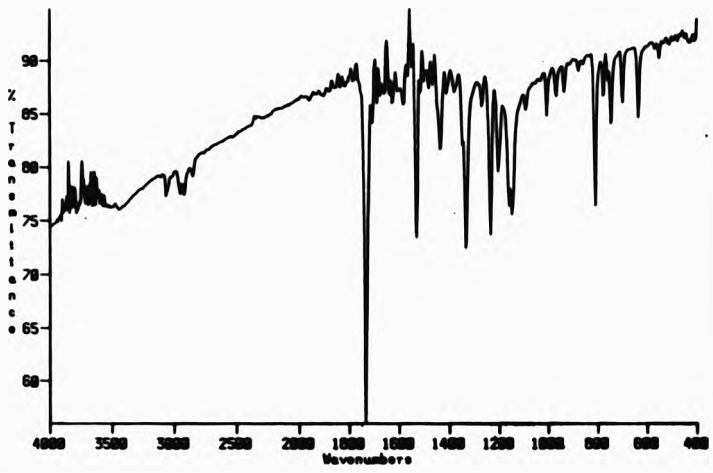


Fig. 3.19 Electron Impact Mass Spectrum of 1,3-Naphthoxazol-2-carboxylate (22)

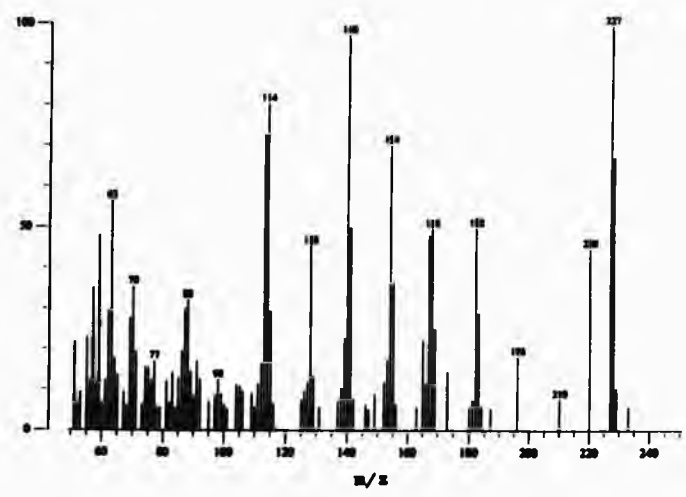
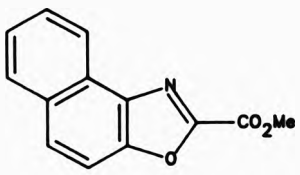


Table 3.15 Relative Abundances of Ions in the Mass Spectrum of 1,3-Naphthoxazole-2-carboxylate (22)

Ion Assignment	Relative Abundance (%)	m/z
$[M]^{+\cdot}$	100	227
$[M - MeO^{\cdot}]^{+}$	22	196
$[M - CO_2]^{+\cdot}$	50	183
$[M - MeCO_2^{\cdot}]^{+}$	42	168



(22)

Previously, 1,3-naphthoxazole-2-carboxylate was obtained by the oxidation of 1,4-naphthoxazine (14) in the presence of $Cu(1\text{-nqo})_2$.[10] Therefore it is reasonable to assume that its formation from the system Cu(1-nqo)/MP involves oxidation of the 1,4-naphthoxazine (20/21).

Significantly, when 1,4-naphthoxazine (20/21) was heated under reflux in the presence of catalytic amounts of $Cu(1\text{-nqo})_2$, 1,3-naphthoxazole-2-carboxylate (22) resulted in high yield.

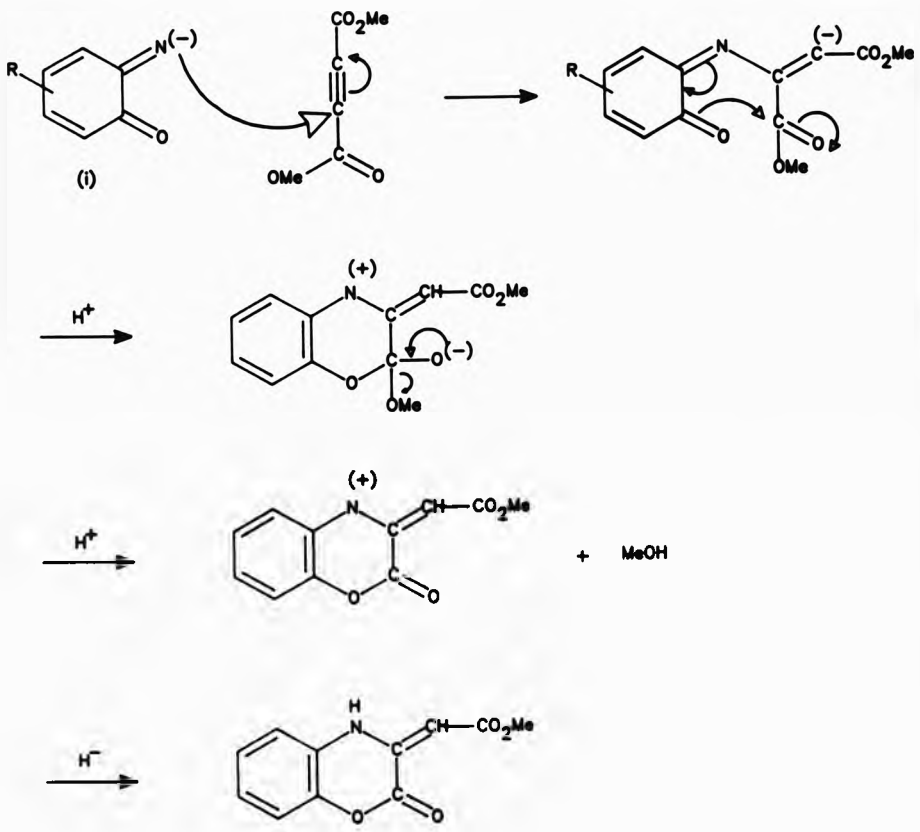
3.4 Mechanistic Appraisal of the Reactions

The reactions of dimethyl acetylenedicarboxylate and methyl propiolate with quinone mono-oximato complexes leads to two types of product, the 1,4-oxazine (16) and the 1,4-benzoxazinone (17) derivatives. This is not entirely unexpected, because in dimethyl acetylenedicarboxylate there are potentially two different electropholic sites. As indicated in Fig. 3.20 these sites are the acetylenic (α) and the carboxylic (β) carbon atoms.

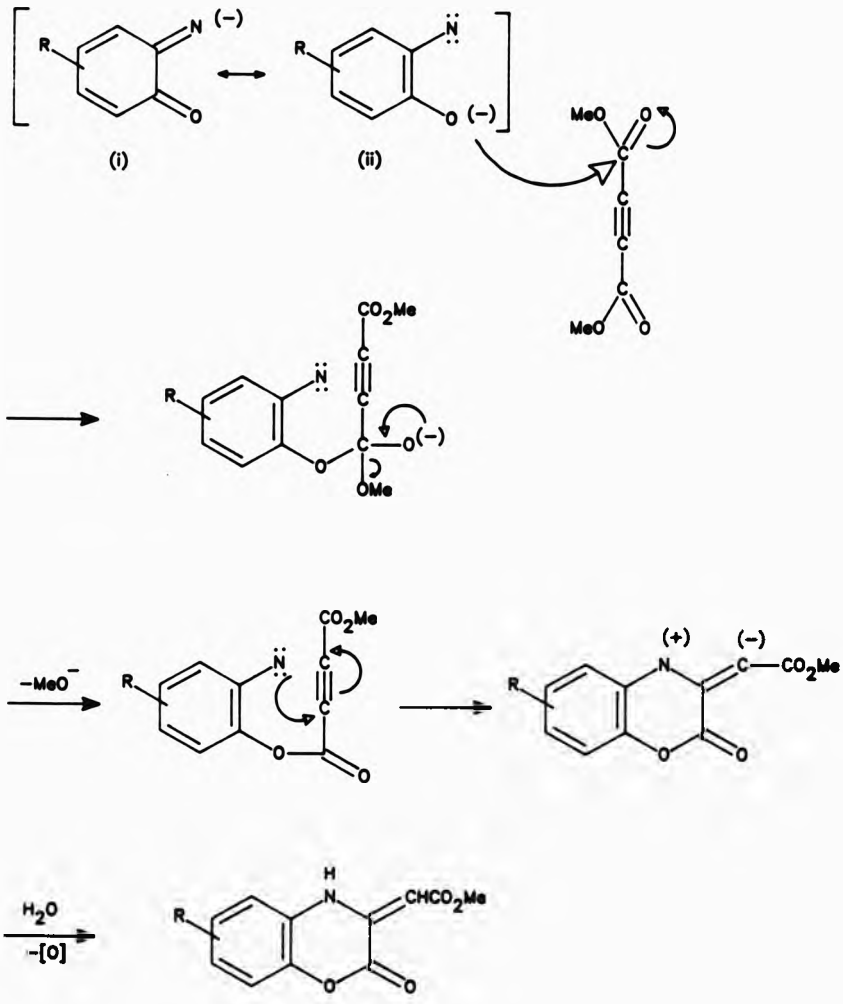
Fig. 3.20

The formation of the 1,4-oxazine derivatives is a simple Diels-Alder 4 + 2 cycloaddition[5] involving the polarized quinone oximic ligand.

The formation of 1,4-benzoxazinone may be rationalised as presented in Schemes 3.10 and 3.11. In both cases, deoxygenation of the quinoneoximic/nitrosophenolic anion is assumed to occur prior to the attack on the



Scheme 3.10



Scheme 3.11

dienophile. In the first proposal the nucleophilic substitution involves the quinone imine anion (i in Scheme 3.10) which attacks the acetylenic carbon atom (C_α). In the other proposal the reaction is assumed to involve the nitrene anion (ii in Scheme 3.11) which attacks the carboxylic carbon atom (C_β). Both mechanisms assume involvement of water and the occurance of redox processes.

The proposed deoxygenation was assumed to be the result of the interaction of the multiple (acetylenic) bond system with a potentially labile oxygen. To examine this hypothesis, the reaction was carried out in the presence of octene.[19] In this case it was found that the only product arising from the reaction mixture is the 1,4-benzoxazinone (17, R = 6-Br) suggesting that the C – C multiple bond is involved probably via the formation of an epoxy species.

Deoxygenation of quinone mono-oximes has previously been observed in reactions of their copper(II) complexes with triphenyl phosphine and amines.[12,20] These reactions lead to the formation of the corresponding 1,4-benzoxazinones, aminophenols, phenazines and phenylimines. Deoxygenation of other aromatic nitroso compounds has also been reported to occur by low valent titanium complexes.[21]

3.5 Single Crystal X-Ray Structure of 6-Bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one

3.5.1 Crystal Data for 6-Bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one

$C_{11}H_8BrNO_4$, M = 298.09, a = 13.785, b = 4.340, c = 18.072 Å, $\alpha = \gamma = 90.00^{\circ}$, $\beta = 92.33^{\circ}$, U = 1080.3 $Å^3$, F(000) = 592.00, μ(Mo-K_α) = 37 cm^{-1}, Z = 4, D_c = 2.03 g cm^{-1}.

3.5.2 Crystal Preparation and Data Collection

6-Bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoquinon-2-one was isolated from the Ni(4-Brqo)$_2$/DMAD system and was recrystallised from a mixture of dichloromethane and acetone to give needle like crystals. The crystal selected for the X-ray study had the dimensions of 0.46 X 0.22 X 0.10 mm. The data were collected on a Philips PW1100 diffractometer in the range $3^{\circ} \leq \theta \leq 25^{\circ}$, with a scan width of $0.9 - 0.01^{\circ}$.[22] Using a graphite monochromated source, a total of 1021 unique reflections with $I/\sigma(I) > 3$ were collected. The intensity relationship $I_{hkl} = I_{\bar{h}kl} = I_{h\bar{k}l} = I_{\bar{h}\bar{k}l}$ observed for selected strong reflections confirmed the presence of a primitive monoclinic crystal system.

3.5.3 Structure Solution and Refinement

Systematic absences in the data of the type: 0k0; K = 2n + 1 and h0l; l = 2n + 1 indicated a space group $P2_1/c$. This was confirmed by complete structure solution in this space group.[23] The coordinates of the bromine atom were deduced from a patterson synthesis, and the remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. The hydrogen atoms attached to nitrogen and carbon atoms were located in a difference Fourier synthesis calculated using data with $\sin\theta < 0.35$. These were included in the structure factor calculations with thermal factors of 0.08 $Å^2$ which refined to 0.09 and 0.04 Å for the nitrogen, phenyl and methyl hydrogens respectively. Absorption correction were applied to the data after initial isotropic refined parameters for all atoms. The nitrogen and bromine atoms were assigned anisotropic thermal parameters in the final cycle of full-matrix refinement which converged to $R = 0.0557$ $(R = \Sigma[F_o - F_c]/\Sigma[F_o])$, and $R_w = 0.0515$ $(R_w = \Sigma[F_o - F_c]W^{1/2}/\Sigma[F_o]W^{1/2})$, with weights of $w = 1/\sigma^2F_o$ assigned to the individual reflections.

All atomic coordinates, temperature factors, structure factors, bond lengths and intra bond angles are given in Appendix 2.

3.5.4 Results and Discussion

Selected bond lengths and bond angles for 6-bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one are shown in Fig 3.21 and Fig 3.22 respectively.

The phenyl ring has a mean bond length of 1.381 Å which is in good agreement with those usually accepted (e.g. 1.387 - 1.410 Å).[24] The C(1) – Br bond length of 1.896 Å is within the range for the para substituted bromophenyl groups (e.g. 1.915 Å).[25] In the 1,4-oxazinone ring, the bond distances C(3) – N [1.371(15) Å] and C(4) – O [1.386(13) Å] are also very similar to those reported previously (Table 3.16). However the C – C single bond distances differ significantly from the standard value of 1.53 Å.[26] The shortened value of 1.483(17) Å for the C(7) – (8) and 1.441(18) Å for the C(9) – C(10) bonds can be explained by the conjugation of the adjacent double bonds i.e. C = O and C = C. Similarly, C(11) – O(4) bond has a normal length of 1.445(16) Å while the C(10) – O(4) bond is shorter by proximity of the double bond to 1.345(16) Å. Such behaviour has also been observed in other related structures.[24,27,28] A comparison of the bond length of the CO groups attached to the oxazinone ring under discussion, to those tabulated for compounds with established 1,4-benzoxazinone structure in Table 3.16 shows that the bond C(7) – O(2)

Table 3.16 Reported Bond Lengths in Oxazinones, Oxazines, Phenazines and Phenothiazines

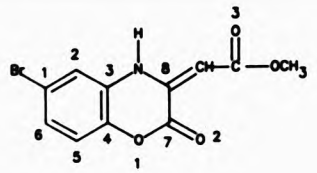
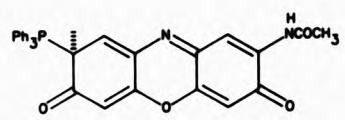
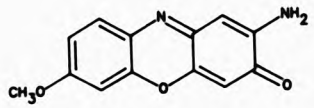
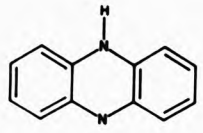
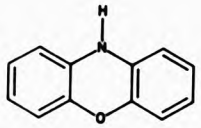
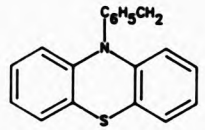
Compound	Bond Length (Å)						
	C(3)–N	C(8)–N	C(4)–O	C(7)–O(1)	C–O(2)	C–O(3)	Ref.
	1.37	1.36	1.38	1.37	1.18	1.22	•
	1.38	1.32	1.35	1.39	1.22	1.27	29
	1.37	1.32	1.37	1.38	1.23	-	30

Table 3.16 cont.

Compound	Bond length (Å)						
	C(3)–N	C(8)–N	C(4)–O	C(7)–O(1)	C–O(2)	C–O(3)	Ref.
	1.34	1.35	-	-	-	-	31
	-	-	1.35	1.34	-	-	32
	1.41	1.41	-	-	-	-	32, 33

* = This work

Fig. 3.21 Selected Bond Lengths in 6-Bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one

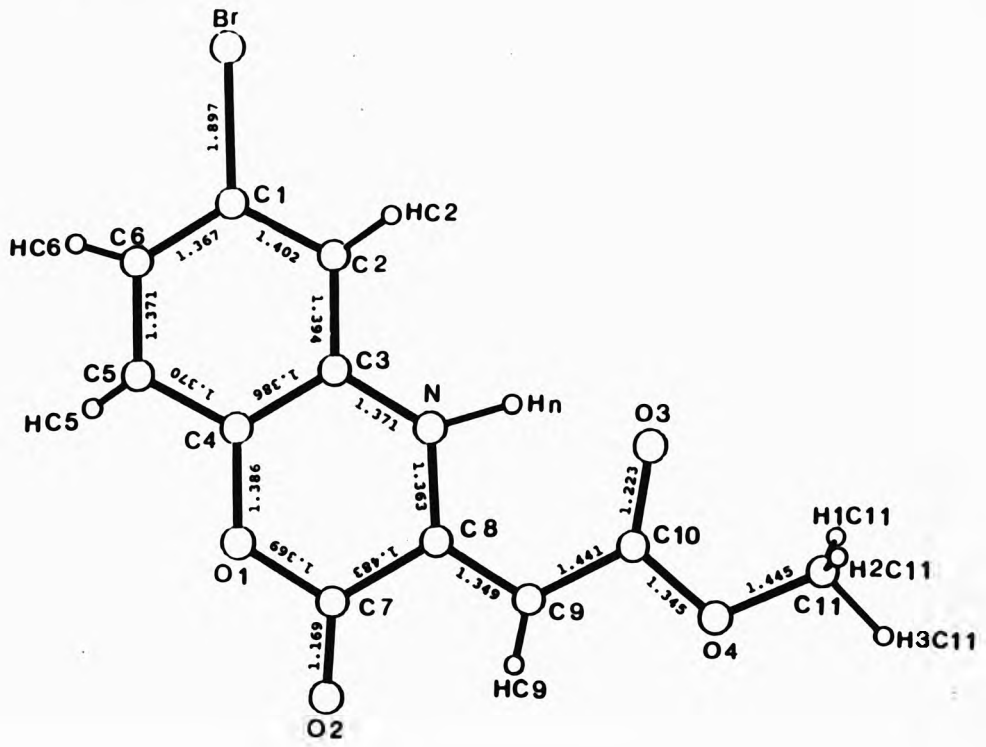
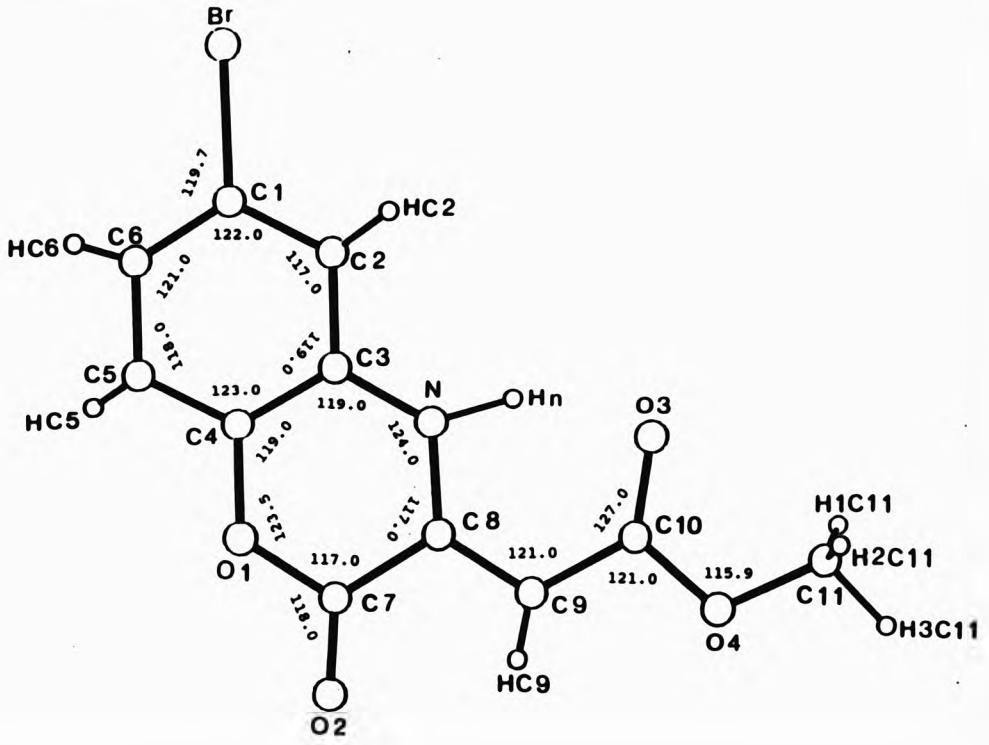


Fig. 3.22 Selected Bond Angles in 6-Bromo-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazine-2-one



[(1.169(16) Å)] is within the quoted range. Significantly, in the structure determined the ring C=O has similar bond length to the C=O [(1.223(15) Å)] of the carbomethoxy group.

The endocyclic bond angles of the 1,4-benzoxazinone (Fig 3.22) ring range from 117.0(1) - 123.5(9)° these values do not deviate significantly from the expected value of 120°. Such a range in the bond angle may be a result of the slight puckering of the ring system. Table 3.17 gives the deviation of all atoms from two planes. In addition the short contact distance Hn...O(3) [1.87 Å] confirms the presence of an intramolecular hydrogen bond.

Table 3.17 Least Square Planes for 6-Bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2one

Atom	Plane 1	Plane 2
C(1)	0.0047*	0.0971
C(2)	-0.0003*	0.0658
C(3)	-0.0052*	0.0145*
C(4)	0.0064*	0.0085*
C(5)	-0.0020*	0.0263
C(6)	0.0037*	0.0701
C(7)	0.0880	0.0146*
C(8)	0.0622	0.0082*
C(9)	0.1297	0.0468
Hn	0.2371	0.2336
H(2)	-0.2134	-0.1394
H(5)	-0.2842	-0.2744
H(6)	-0.2050	-0.1168
H(7)	0.1336	-0.0255
H(11a)	0.7305	0.6570
H(11b)	-0.5146	-0.5930
H(11c)	0.1841	0.0679
Br	0.0697	0.2252
N	-0.0123	-0.0195*
O(1)	0.0297	-0.0210*
O(2)	0.1577	0.0399
O(3)	0.1602	0.1413
O(4)	0.2151	0.1232

*=Atoms included in the calculations of the Least square-planes

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CHAPTER FOUR

EXPERIMENTAL

4.1 Reagents and General Techniques

The reagents used were obtained commercially and used without further purification. Solvents for column chromatography were freshly distilled. The silica gel absorbent used in the chromatography columns was Merck silica gel 60 (70-230 mesh) supplied by BDH Chemicals Limited. Thin layer chromatography was performed using precoated Merck Kieselgel 60 F_{254} plates [Solvent system used for t.l.c.: Cl_2CH_2(10), EtAc(6), MeOH(2), and Toluene(1)].

Preparation of Hydroxylamine.- To absolute ethanol at -10 °C, hydroxylamine hydrochloride (1 mol equiv.) and sodium metal (1 mol equiv.) were added with stirring (1/2h). The precipitated sodium chloride was removed by filtration to give a clear solution of hydroxylamine.

4.2 Analytical Techniques

Copper, nickel, cobalt, and manganese in the samples of metal complexes were determined quantitatively by the method of atomic absorption spectrometry, using a Pye-Unicam SP9 atomic absorption spectrometer. Wet oxidation was achieved by heating a known mass (*ca.* 0.1 g) of the material in concentrated nitric acid (*ca.* 4-8 cm^3) and subsequent addition of hydrogen peroxide

(30%, *ca.* 1-3 cm^3). After allowing the mixture to digest, the inorganic residue was diluted to a known volume with water. Standard solutions were prepared using Analar grade metal chlorides.

Carbon, hydrogen and nitrogen analysis were carried out on a Carlo Erba 1106 microanalytical unit.

4.3 Physical Techniques

Thermal Gravimetric Analysis.- Thermal gravimetric analysis was carried out on a Stanton HT-SM Thermobalance. A heating rate of *ca.* 3 °C min^{-1} was used.

Magnetic Measurements.- Room temperature magnetic moments were recorded using a Johnson Matthey magnetic susceptibility balance. The instrument was calibrated with a solution of manganese(II) chloride. The magnetic susceptibility values were corrected for the diamagnetic effect of the metal and the ligands.[1]

Infra-red Spectroscopy.- Infra-red spectra in the region 4000-400 cm^{-1} were recorded on a BIO-RAD FTS40 spectrometer. The samples were prepared as pressed potassium discs.

Mass Spectrometry.- Mass spectra were recorded on a Kratos Profile Spectrometer with a Sun Data Station.

Nuclear Magnetic Resonance Spectroscopy.- Fourier transform ^{1}H and ^{13}C n.m.r. spectra were recorded on a Bruker AM250 or on a Joel 270 and 500 MHz spectrometer. Trimethylsilane was used as reference standard for spectra recorded in d_6-dimethylsulphoxide and deuterated chloroform.

Ultra Violet/Visible Spectroscopy.- U.v./vis. spectra in the region 900-190 nm were obtained using a SUMATZU U.V.-2100 spectrometer.

Melting Points.- All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected.

4.4 Reactions

4.4.1 Nitrosation of 3-Acetylaminophenol at 20 °C

To a mixture of 3-acetylaminophenol (6.9 g, 46 mmol) and sodium nitrite (11.4 g, 17 mmol) in water (70 cm^3), acetic acid (11 cm^3) was added dropwise with stirring (3 h). Filtration gave an orange solid (3.7 g) which was washed with water (5 X 50 cm^3) and dried at 0.1 mm/20 °C to give a solid (solid S1) (Three component by t.l.c.).

Solid S1 (0.54 g) was mixed with silica and chromatographed. Elution with toluene gave acetylaminonitrophenol (0.06 g, 11%) (Found: M^+, 196; C, 48.7; H, 3.8; N, 14.2. $C_8H_8N_2O_4$ requires: M^+, 196; C,

49.0; H, 4.1; N, 14.3%). Further elution with toluene-ethyl acetate (9:1) gave 5-acetylamino-1,4-benzoquinone 4-oxime (0.1 g, 19%) (Found: M^+, 180; C, 53.2; H, 4.4; N, 15.5. Calc. for $C_8H_8N_2O_3$: M^+, 180; C, 53.3, H, 4.4; N, 15.6%). Final elution with toluene-ethyl acetate (7:3) gave 5-acetylamino-1,2-benzoquinone 2-oxime (0.37 g, 69%) (Found: M^+, 180; C, 53.1; H, 4.2; N, 15.4. Calc. for $C_8H_8N_2O_3$: M^+, 180; C, 53.3; H, 4.4; N, 15.6%).

4.4.2 Nitrosation of 3-Acetylaminophenol at -10 °C

To a mixture of 3-acetylaminophenol (14.1 g, 94 mmol) and sodium nitrite (9.4 g, 14 mmol) in water (140 cm^3) at -10 °C, acetic acid (14 cm^3) was added dropwise with stirring (3 h). Filtration gave an orange solid which was washed with water (5 X 100 cm^3), diethyl ether (5 x 50 cm^3) and dried at 0.1 mm/20 °C to give 5-acetylamino-1,2-benzoquinone 2-oxime (14.7 g, 83%) (Found: M^+, 180; C, 53.1; H, 4.2; N, 15.4. Calc. for $C_8H_8N_2O_3$: M^+, 180; C, 53.3; H, 4.4; n, 15.6%).

4.4.3 Nitrosation of 3-Acetylaminophenol in Presence of Copper(II) Sulphate Pentahydrate

Copper(II) sulphate pentahydrate (6.4 g, 26 mmol) in water (50 cm^3) was added to a solution of 3-acetylaminophenol (7.7 g, 51 mmol), acetic acid (15 cm^3) and sodium acetate trihydrate (15.0 g,

109 mmol) in methanol-water (75 cm^3, 2:1). Sodium nitrite (8.5 g, 123 mmol) in water (50 cm^3) was added dropwise (1 h) and the mixture was stirred (24 h). Filtration gave a brown solid which was washed with water (3 X 150 cm^3), methanol (3 X 15 cm^3), and extracted (Soxhlet) with ethyl acetate. The brown residue was then dried at 0.1 mm/20 °C to give *bis(5-acetylamino-1,2-benzoquinone 2-oximato)copper(II)* (9.8 g, 90%), m.p. 240-250 °C (decomp.), μ_B 2.0 (Found : C, 45.7; H, 3.4; Cu, 14.9; N, 13.2. $C_{16}H_{14}CuN_4O_6$ requires : C, 45.6; H, 3.3; Cu, 15.0; N, 13.3%). Concentration of the extract to low volume gave yellow crystalline 3-acetylamino-1,4-benzoquinone 4-oxime (0.35 g, 8%), m.p. 190 °C (decomp.) (Found: C, 52.9; H, 4.3; N, 15.7. Calc. for $C_8H_8N_2O_2$: C, 53.0; H, 4.4; N, 15.6%).

4.4.4 Reaction of 5-Acetylamino-1,2-benzoquinone 2-oxime with Copper(II) Chloride Dihydrate in Methanol

To a solution of copper(II) chloride dihydrate (1.5 g, 8.6 mmol) in methanol (50 cm^3), solid 5-acetylamino-1,2-benzoquinone 2-oxime (3.0 g, 17 mmol) was added with stirring (24 h). The dark brown solution obtained was dried under nitrogen to give a brown solid. After washing with water (3 X 50 cm^3), ethyl acetate (3 X 50 cm^3) and drying at 0.1 mm/20 °C, bis(5-acetylamino-1,2-benzoquinone 2-oximato)copper(II) (2.9 g, 83%) m.p. 240-250 C° (decomp.), μ_B 2.0 (Found:

C, 44.6; H, 3.3; Cu, 14.9; N, 13.2. Calc. for $C_{16}H_{14}CuN_4O_9$: C, 45.54; H, 3.3; Cu, 15.1; N, 13.3%) was obtained.

4.4.5 Interaction of Bis(5-acetylamino-1,2-benzoquinone 2-oximato)copper(II) with Pyridine

To a suspension of bis(5-acetylamino-1,2-benzoquinone 2-oximato)copper(II) (0.5 g, 1.2 mmol) in acetone (40 cm^3), pyridine (0.4 g, 4.8 mmol) was added at 20 °C with stirring (24 h). Filtration gave a coffee coloured solid which was washed with light petroleum (b.p. 30-40 °C) (3 x 50 cm^3) and dried at 0.1 mm/20 °C to give *bis(5-acetylamino-1,2-benzoquinone 2-oximato)-bis(pyridine)copper(II)* (0.6 g, 90%) m.p. 240-250 °C (decomp.), μ_B 1.9 (Found: C, 53.9; H, 4.1; Cu, 10.8; N, 14.8. $C_{26}H_{24}CuN_6O_6$ requires: C, 53.8; H, 4.1; Cu, 11.0; N, 14.5%).

4.4.6 Pyrolysis of Bis(5-acetylamino-1,2-benzoquinone 2-oximato)bis(pyridine)copper(II)

Bis(5-acetylamino-1,2-benzoquinone 2-oximato)bis-(pyridine)copper(II) (1.4565 g) was heated at 0.1 mm/150-190 °C (3 h). The brown residue was bis(5-acetylamino-1,2-benzoquinone 2-oximato)copper(II) (1.0077 g, 95%) (confirmed by comparative i.r. with an authentic sample *cf.* 4.4.3).

4.4.7 Interaction of Bis(5-acetylamino-1,2-benzoquinone 2-oximato)copper(II) with 2,2′-Dipyridyl

To a suspension of bis(5-acetylamino-1,2-benzoquinone 2-oximato)copper(II) (2.0 g, 4.7 mmol) in acetonitrile (70 cm^3), 2,2′-dipyridyl (1.5 g, 9.7 mmol) was added. The mixture was stirred at 20 °C for 24 h. Filtration afforded a brown solid, which was washed with acetone and dried at 0.1 mm/20 °C to give *bis(5-acetylamino-1,2-benzoquinone 2-oximato)(2,2′-dipyridyl)copper(II)* (2.6 g, 95%), m.p. 220-240 °C (decomp.), μ_s 1.79 (Found: C, 54.0; H, 3.8; Cu, 10.4; N, 14.6. $C_{26}H_{22}CuN_6O_6$ requires: C, 54.0; H, 3.8; Cu, 11.1; N, 14.6%).

4.4.8 Interaction of Bis(5-acetylamino-1,2-benzoquinone 2-oximato)copper(II) with Hydroxylamine

To a suspension of bis(5-acetylamino-1,2-benzoquinone 2-oximato)copper(II) (0.8 g, 1.9 mmol) in absolute ethanol (60 cm^3) at -20 °C, hydroxylamine (0.2 g, 5.4 mmol) in absolute ethanol (40 cm^3) at -10 °C was added. The reaction mixture was stirred at -20 °C (4 h). Filtration afforded the unreacted complex (0.78 g, 96% recovery) (confirmed by comparative i.r. with an authentic sample *cf.* 4.4.3).

4.4.9 Nitrosation of 3-Acetylaminophenol in the Presence of Nickel(II) Chloride Hexahydrate

Nickel(II) chloride hexahydrate (6.0 g, 25 mmol) in water (50 cm^3) was added to a solution of 3-acetylaminophenol (7.6 g, 45 mmol), acetic acid (15 cm^3) and sodium acetate trihydrate (15.0 g, 109 mmol) in methanol-water (75 cm^3, 2:1). Sodium nitrite (8.5 g, 123 mmol) in water (50 cm^3) was added dropwise (1 h). The mixture was then stirred (24 h). Filtration gave an orange solid which was washed with water (3 x 150 cm^3), methanol (3 x 15 cm^3), and extracted (Soxhlet) with ethyl acetate to give orange *bis(5-acetylamino-1,2-benzoquinone 2-oximato)nickel(II) hexahydrate* (11.6 g, 87%), m.p. 250-260 °C (decomp.), μ_B 3.0 (Found: C, 36.1; H, 4.9; Ni, 11.2; N, 10.5. $C_{16}H_{26}N_4NiO_{12}$ requires: C, 36.6; H, 5.0; Ni, 11.2; N, 10.7%). Concentration of the extract to low volume gave yellow 3-acetylamino-1,4-benzoquinone 4-oxime (0.5 g, 10.6%), m.p. 190 °C (decomp.) (Found: C, 52.9; H, 4.4; N, 15.7. Calc. for $C_8H_8N_2O_2$: C, 53.0; H, 4.4; N, 15.6%) which was filtered off and dried at 0.1 mm/20 °C.

4.4.10 Pyrolysis of Bis(5-acetylamino-1,2-benzoquinone 2-oximato)nickel(II) Hexahydrate

Bis(5-acetylamino-1,2-benzoquinone 2-oximato)nickel(II) hexahydrate (1.1176 g) was heated at 0.1 mm/100-120 °C (2 h). The brown residue was

bis(5-acetylamino-1,2-benzoquinone 2-oximato)nickel(II), (0.8943 g, 87%) m.p 250-260 °C (decomp.), μ_B 1.11 (Found: C, 45.5; H, 4.0; N, 14.0; Ni, 14.1. $C_{16}H_{14}N_4NiO_6$ requires C, 46.0; H, 3.4; Ni, 14.0; N, 13.5%).

4.4.11 Reaction of 5-Acetylamino-1,2-benzoquinone 2-oxime with Nickel(II) Chloride Hexahydrate in Aqueous Acetic Acid

To a solution of nickel(II) chloride hexahydrate (1.4 g, 5.8 mmol) in acetic acid-water (50 cm^3, 1:1), solid 5-acetylamino-1,2-benzoquinone 2-oxime (2.0 g, 11 mmol) was added with stirring (3 h). Filtration gave an orange solid which was washed with water (3 X 50 cm^3), and ethyl acetate (3 X 50 cm^3) to give bis(5-acetylamino-1,2-benzoquinone 2-oximato)-nickel(II) hexahydrate (2.0 g, 87%), m.p. 250-260 °C (decomp.) , μ_B 3.0 (Found: C, 36.1; H, 4.9; Ni, 11.2; N, 10.5. Calc. for $C_{16}H_{26}NiN_4O_{12}$: C, 36.6; H, 5.0; Ni, 11.2; N, 10.7%)

4.4.12 Reaction of 5-Acetylamino-1,2-benzoquinone 2-oxime with Nickel(II) Chloride Hexahydrate in Methanol

To a solution of nickel(II) chloride hexahydrate (1.3 g, 5.4 mmol) in methanol (50 cm^3) solid 5-acetylamino-1,2-benzoquinone 2-oxime (2.0 g, 11 mmol) was added with stirring (3 h). The resultant brown-red solution was dried under nitrogen to give a brown

residue. The latter was washed with water (3 X 50 cm^3), ethyl acetate (3 X 50 cm^3) and dried at 0.1 mm/20 °C to give a solid (solid S1) (1.8 g), m.p. 250-260 °C (decomp.), μ_B 3.0 (Found: C, 34.1; H, 3.8; Ni, 11.2; N, 10.4%).

To a suspension of S1 (0.5 g) in acetone (40 cm^3), pyridine (0.4 g, 4.8 mmol) was added at 20 °C with stirring (24 h). Dropwise addition of the resultant viscous orange solution to light petroleum ether (b.p. 30-40 °C) (100 cm^3) gave an orange precipitate. this was filtered off, washed with light petroleum (b.p. 30-40 °C) (3 X 50cm^3) and dried at 0.1 mm/20 °C to give *bis(5-acetylamino-1,2-benzoquinone 2-oximato)bis-(pyridine)nickel(II)* (0.62 g, 90%), m.p. 250-260 °C (decomp.), μ_B 3.0 (Found: C, 54.2; H, 4.3; Ni, 9.8; N, 14.5. $C_{26}H_{24}N_6NiO_6$ requires: C, 54.3; H, 4.2; Ni, 10.3; N, 14.6%).

4.4.13 Interaction of Bis(5-acetylamino-1,2-benzoquinone 2-oximato)nickel(II) with Pyridine

To a suspension of *bis(5-acetylamino-1,2-benzoquinone 2-oximato)nickel(II)* (0.5 g, 1.2 mmol) in acetone (40 cm^3), pyridine (0.4 g, 4.8 mmol) was added at 20 °C with stirring (24 h). Dropwise addition of the resultant viscous orange solution, to light petroleum (b.p. 30-40 °C) (100 cm^3), gave an orange precipitate. This was filtered off, washed with light petroleum

(b.p. 30-40 °C) (3 x 50 cm^3) and dried at 20 °C/0.1 mm to give bis(5-acetylamino-1,2-benzoquinone 2-oximato)-bis(pyridine)nickel(II) (0.65 g, 94%), μ_B 3.0 (Found: C, 54.2; H, 4.3; Ni, 9.8; N, 14.5. Calc. for $C_{26}H_{24}NiN_6O_6$:C, 54.3; H, 4.2; Ni, 10.3; N, 14.6%).

4.4.14 Interaction of Bis(5-acetylamino-1,2-benzoquinone 2-oximato)nickel(II) with 2,2'-Dipyridyl

To a suspension of bis(5-acetylamino-1,2-benzoquinone 2-oximato)nickel(II) (2.1 g, 4.0 mmol) in acetonitrile (70 cm^3), 2,2'-dipyridyl (1.5 g, 9.5 mmol) was added. The mixture was stirred at 20 °C for 24 h. Filtration gave a red solid which was washed with acetone and dried at 0.1 mm/20 °C to give *bis(5-acetylamino-1,2-benzoquinone 2-oximato)(2,2'-dipyridyl)nickel(II)* (2.0 g, 95%), m.p. 260-270 °C (decomp.), μ_B 2.98 (Found: C, 54.7; H, 3.9; Ni, 10.1; N, 14.7. $C_{26}H_{22}NiN_6O_6$ requires: C, 54.5, H, 3.8; Ni, 10.3; N, 14.7%).

4.4.15 Interaction of Bis(5-acetylamino-1,2-benzoquinone 2-oximato)nickel(II) with Hydroxylamine

To a suspension of bis(5-acetylamino-1,2-benzoquinone 2-oximato) (0.8 g, 1.9 mmol) in absolute ethanol (60 cm^3) at -20 °C, hydroxylamine (0.16 g, 4.9 mmol) in absolute ethanol (40 cm^3) at -10 °C was added. An immediate colour change from orange to deep red was

observed. The reaction mixture was left to stir at -20 °C (4 h). Filtration afforded a red solid which was washed with water (3 X 5 cm^3), ethanol (3 X 10 X cm^3) and dried at 0.1 mm/20 °C to give *bis(5-acetylamino-1,2-benzoquinone 2-oximato)bis-(hydroxylamine)nickel(II)* (0.8 g, 87%), m.p. 250-260 °C (decomp.), μ_B 2.9 (Found: C, 39.9; H, 4.3; Ni, 12.1; N, 17.6. $C_{16}H_{20}NiN_6O_8$ requires: C, 39.8, H, 4.2; Ni, 12.2; N, 17.4%).

4.4.16 Nitrosation of 3-Acetylaminophenol in the Presence of Cobalt(II) Chloride Hexahydrate

Cobalt(II) chloride hexahydrate (11.4 g, 48 mmol) in water (50 cm^3) was added to a solution of 3-acetylaminophenol (14.6 g, 97 mmol), acetic acid (30 cm^3) and sodium acetate trihydrate (30.0 g, 217 mmol) in methanol-water (300 cm^3, 2:1). Sodium nitrite (18.0 g, 259 mmol) in water (100 cm^3) was then added dropwise (1 h) and the mixture was stirred (24 h). Concentration of the resultant red solution under nitrogen and filtration gave a black solid which was washed with water (3 X 150 cm^3), ethyl acetate (2 X 25 cm^3), and extracted (Soxhlet) with diethyl ether. The black residue was dried at 0.1 mm/20 °C to give, *penta(5-acetylamino-1,2-benzoquinone 2-oximato)-μ-peroxo-dicobaltate(III)* (11.0 g, 54%), m.p. 260-270 °C (decomp.), (Found: C, 45.9; H, 3.3; Co, 11.2; N, 13.4. $C_{40}H_{36}Co_2N_{10}O_{16}$ requires: C, 45.9; H, 3.3; Co, 10.2; N,

13.4%). Concentration of the ether extract to low volume gave a mixture of 3-acetylamino-1,4-benzoquinone 4-oxime and 5-acetylamino-1,2-benzoquinone 2-oxime (2.5 g, 43%) (confirmed by comparative t.l.c. with authentic samples *cf.* 4.4.1)

In another experiment cobalt(II) chloride hexahydrate (11.4 g, 47.5 mmol) in water (50 cm^3) was added to a solution of 3-acetylaminophenol (14.5 g, 97 mmol), sodium acetate trihydrate (30.0 g, 217 mmol), acetic acid (30 cm^3) in methanol-water (300 cm^3, 2:1). This was followed by the one step addition of sodium nitrite (17.0 g, 245 mmol) in water (100 cm^3) and stirring (24 h). The concentration of the resultant red solution under nitrogen followed by filtration afforded 3-acetylaminophenol (12.0 g, 83% recovery) (confirmed by comparative i.r.). Further concentration of the filtrate gave an orange solid (9.2 g) (Found: C, 0.8; H, 0.7; Co, 22.1; N, 9.3%) which was washed with acetone and dried at 0.1 mm/20 °C.

4.4.17 Nitrosation of 3-Acetylaminophenol in the Presence of Sodium Hexanitrocobaltate(III)

To a solution of sodium hexanitrocobaltate(III) (9.5 g, 23.5 mmol) and sodium acetate trihydrate (15.5 g, 11.2 mmol) in water-acetic acid (150 cm^3, 10:1), solid 3-acetylaminophenol (7.1 g, 47 mmol) was added. Methanol (200 cm^3) was then added to dissolve all the phenol.

Sodium nitrite (9.9 g, 14.3 mmol) in water (50 cm^3), was added dropwise (1 h) and the mixture was stirred (24 h). A deep red solution was obtained which was concentrated to a third of its volume under nitrogen. Filtration afforded a black solid which was washed with water (1 X 10 cm^3), extracted (Soxhlet) with diethyl ether and dried at 0.1 mm/20 °C to give *sodium dinitrobis(5-acetylamino-1,2-benzoquinone 2-oximato)-cobaltate(III)* (10.5 g, 81%), m.p 190-200 °C (decomp.) (Found: C, 36.8; H, 3.32; Co, 11.3; Na, 4.5; N, 15.1. $C_{16}H_{16}CoNaN_6O_{10}$ requires: C, 36.1; H, 2.6; Co, 11.1; Na, 4.3; N, 15.8%). Concentration of the extract afforded 5-acetylamino-1,2-benzoquinone 2-oxime (0.1 g, 1%) (confirmed by comparative t.l.c. with an authentic sample *cf.* 4.4.1)

4.4.18 Reaction of 5-Acetylamino-1,2-benzoquinone 2-oxime with Cobalt(II) Chloride Hexahydrate in Methanol

To a solution of cobalt(II) chloride hexahydrate (0.8 g, 3.3 mmol) in methanol (40 cm^3), solid 5-acetylamino-1,2-benzoquinone 2-oxime (2.1 g, 1.2 mmol) was added and the mixture was stirred (3 h). The resultant red solution was dried under nitrogen to give a red solid which was washed with water (4 X 100 cm^3), extracted (Soxhlet) with diethyl ether and dried at 0.1 mm/20 °C to give *tris(5-acetylamino-1,2-benzoquinone 2-oximato)cobaltate(III)* (2.0 g, 91 %) m.p. 290-300 °C (Found: C, 47.9; H, 3.8; Co, 9.1; N, 14.2. $C_{24}H_{21}CoN_6O_9$

requires: C, 48.3; H, 3.5; Co,9.9; N,14.1%). (four component by t.l.c. with Rf values of 0.39, 0.32, 0.24, and 0.26).

4.4.19 Reaction of 5-Acetylamino-1,2-benzoquinone 2-oxime with Cobalt(II) Chloride Hexahydrate in Acetic Acid-Methanol Mixture

To a solution of cobalt(II) chloride hexahydrate (1.2 g, 5 mmol) in acetic acid-methanol (50 cm^3, 1:1), solid 5-acetylamino-1,2-benzoquinone 2-oxime (2.7 g, 15 mmol) was added with stirring (3 h). Filtration afforded a red solid which was washed with water (4 X 100 cm^3), diethyl ether (4 X 100 cm^3) and dried at 0.1 mm/20 °C to give tris(5-acetylamino-1,2-benzoquinone 2-oximato)-cobaltate(III) (2.5 g, 84%), m.p. 290-300°C (decomp.) (Found: C, 47.9; H, 3.9; Co, 9.9; N, 14.0. Calc. for $C_{24}H_{21}CoN_6O_9$: C, 48.3; H, 3.5; Co, 9.9; N, 14.1%) (two component by t.l.c. with Rf values of 0.39 and 0.32).

4.4.20 Reaction of 5-Acetylamino-1,2-benzoquinone 2-oxime with Cobalt(II) Chloride Hexahydrate in Acetic Acid-Water Mixture

To a solution of cobalt(II) chloride hexahydrate (1.6 g, 4.9 mmol) in acetic acid-water (50 cm^3, 1:1), solid 5-acetylamino-1,2-benzoquinone 2-oxime (3.2 g, 17.8 mmol) was added with stirring (3 h). Filtration of

the mixture afforded a red solid, which was washed with water (4 X 100 cm^3), diethyl ether (4 X 100 cm^3) and then dried at 0.1 mm/20 °C to give tris(5-acetylamino-1,2-benzoquinone 2-oximato)-cobaltate(III) (2.5 g, 85%), m.p. 290-300 °C (decomp.) (Found: C, 47.9; H, 3.9; Co, 9.9; N, 14.0. Calc. for $C_{24}H_{21}CoN_6O_9$: C, 48.3; H, 3.5; Co, 9.9; N, 14.1%) (two component by t.l.c. with Rf values of 0.39 and 0.32).

4.4.21 Reaction of Excess 5-Acetylamino-1,2-benzoquinone 2-oxime with Sodium Hexanitrocobaltate(III)

To a solution of sodium hexanitrocobaltate(III) (0.5 g, 1.2 mmol) in methanol-water (50 cm^3, 1:1), solid 5-acetylamino-1,2-benzoquinone 2-oxime (1.0 g, 5.6 mmol) was added with stirring (48 h). Filtration gave a red solid which was washed with water (2 X 100 cm^3), dichloromethane (4 X 50 cm^3) and dried at 0.1 mm/20 °C to give tris(5-acetylamino-1,2-benzoquinone 2-oximato)cobaltate(III) (0.6 g, 83.3%), m.p. 290-300 °C (decomp.) (Found: C, 48.0; H, 3.7; Co, 9.9; N, 14.0. Calc. for $C_{24}H_{21}CoN_6O_9$: C, 48.3; H, 3.5; Co, 9.9; N, 14.0%) (two component by t.l.c. with Rf values of 0.39 and 0.32).

4.4.22 Reaction of 5-Acetylamino-1,2-benzoquinone 2-oxime (2 mol equiv.) with Sodium Hexanitrocobaltate(III) (1 mol equiv.)

To a suspension of 5-acetylamino-1,2-benzoquinone 2-oxime (2.2 g, 12 mmol) in methanol (120 cm^3) sodium hexanitrocobaltate(III) (2.3 g, 6 mmol) in water (20 cm^3) was added potionwise. The resultant red mixture was stirred (12 h) and then concentrated to a third of its volume. Filtration gave a red brown solid which was washed with water (2 X 5 cm^3), methanol (2 X 5 cm^3) and dried at 0.1 mm/20 °C to give a solid (solid S1) (0.41 g) (Found: C, 36.5; H, 2.8; Co, 10.7; Na, 8.2; N, 16.1%). The filtrate was concentrated further to give a lighter colour brown solid (solid S2) (2.2 g) (Found: C, 32.2; H, 2.5; Co, 12.8; Na, 14.9; N, 16.8%).

4.4.23 Reaction of 5-Acetylamino-1,2-benzoquinone 2-oxime with Sodium Hexanitrocobaltate(III) in the Presence of Sodium Nitrite

To a suspension of 5-acetylamino-1,2-benzoquinone 2-oxime (1.1 g, 6.1 mmol) in methanol (70 cm^3), sodium hexanitrocobaltate(III) (1.1 g, 2.7 mmol) and sodium nitrite (3.8 g, 55 mmol) in water (15 cm^3) was added with stirring (24 h). Concentration of the mixture to a third of its original volume and filtration gave a deep red crystalline solid (1.2 g) which by t.l.c. was shown to contain traces of the tris chelate and another less

soluble component. Extraction (Soxhlet) with dichloromethane left a dark residue which was dried at 0.1 mm/20 °C to give a solid (solid S1) (0.9 g) (Found: C, 36.0; H, 2.7; Co, 8.1; Na,7.0; N, 16.4%)

4.4.24 Interaction of Penta(5-acetylamino-1,2-benzoquinone 2-oximato)-μ-peroxo-cobaltate(III) with Pyridine

To a suspension of penta(5-acetylamino-1,2-benzoquinone 2-oximato)-μ-peroxo-dicobaltate(III) (2.0 g, 1.8 mmol) in acetone (120 cm^3), pyridine (3.0 g, 38 mmol) was added with stirring under reflux (10 h). Filtration gave the unreacted complex (1.9 g, 96% recovery) (confirmed by comparative i.r. and elemental analysis with an authentic sample *cf.* 4.4.16)

4.4.25 Interaction of Sodium Dinitrobis(5-acetylamino-1,2-benzoquinone 2-oximato)cobaltate(III) with Pyridine

Sodium dinitrobis(5-acetylamino-1,2-benzoquinone 2-oximato)cobaltate(III) (0.9 g, 1.6 mmol) was refluxed in pyridine (40 cm^3) (12 h). Filtration gave a black solid which was washed with water (2 X 5 cm^3), light petroleum (b.p. 30-40 °C) (7 X 20 cm^3) and dried at 0.1 mm/20 °C to give a solid (solid S1) (0.30 g) (Found: C, 41.1; H, 3.1, Co, 10.1; N, 15.5). The filtrate was dried under nitrogen to give a dark red solid which was washed with water (2 X 5 cm^3), light petroleum ether

(b.p. 30-40 °C) (7 X 20 cm^3) and dried at 0.1 mm/20 °C to give a black solid (solid S2) (0.37 g) (Found: C, 44.9; H, 3.6; Co, 6.8; N, 15.2%).

4.4.26 Interaction of Tris(5-acetylamino-1,2-benzoquinone 2-oximato)cobaltate(III) with Pyridine

To a suspension of tris(5-acetylamino-1,2-benzoquinone 2-oximato)cobaltate(III) (0.5 g, 0.8 mmol) in acetone (50 cm^3), pyridine (1.3 g, 16.7 mmol) was added with stirring under reflux (10 h). Concentration of the mixture to dryness under nitrogen gave a red solid. This was washed with light petroleum (b.p. 30-40 °C) and dried at 0.1 mm/20 °C to give tris(5-acetylamino-1,2-benzoquinone 2-oximato)-cobaltate(III) (0.5 g, 100% recovery) (identified by t.l.c. and comparative i.r. with an authentic sample *cf.* 4.4.19)

4.4.27 Nitrosation of 3-Acetylaminophenol in the Presence of Manganese(II) Chloride Tetrahydrate

Sodium nitrite (16.3 g, 236 mmol) in water (100 cm^3) was added dropwise (1 h) to a mixture of manganese(II) chloride tetrahydrate (9.73 g, 49 mmol), 3-acetylaminophenol (15.1 g, 101 mmol), sodium acetate trihydrate (30.4 g, 220 mmol) in methanol-acetic acid, (330 cm^3, 30:1) and the mixture was stirred (12 h). A thick green mixture resulted which on filtration gave a

black green solid. This was washed with water (4 X 150 cm^3), extracted (Soxhlet) with diethyl ether and dried at 0.1 mm/20 °C to give *tris(5-acetylamino-1,2-benzoquinone 2-oximato)-manganese(III) monohydrate* (4.2 g, 20%), m.p. 250 °C (decomp.), μ_B 2.89 (Found: C, 46.6; H, 3.9; Mn, 8.9; N, 13.6. $C_{24}H_{23}MnN_6O_{10}$ requires: C, 47.2; H, 3.8; Mn, 9.0; N, 13.8%). Concentration of the ether extract gave 5-acetylamino-1,2-benzoquinone 2-oxime (0.4 g, 3%) (confirmed by comparative t.l.c. with an authentic sample *cf.* 4.4.1). Concentration of the filtrate afforded 3-acetylamino-1,4-benzoquinone 4-oxime (1.8 g, 15%) (confirmed by comparative t.l.c. with an authentic sample *cf.* 4.4.1).

In a second experiment sodium nitrite (17.0 g, 246 mmol) in water (100 cm^3) was added in one step to a mixture of manganese(II) chloride tetrahydrate (9.9 g, 50 mmol), 3-acetylaminophenol (14.8 g, 99 mmol), sodium acetate trihydrate (30.2 g, 219 mmol) in methanol-acetic acid, (330 cm^3, 30:1). The mixture was stirred (12 h). Filtration gave a black-green solid which was washed with water (4 X 150 cm^3), extracted (Soxhlet) with diethyl ether and dried at 0.1 mm/20 °C to give tris(5-acetylamino-1,2-benzoquinone 2-oximato) manganese(III) monohydrate (5.6 g, 28%) m.p. 250 °C (decomp.) (confirmed by i.r. and elemental analysis with an authentic sample *cf.* above). Concentration of the extract gave 5-acetylamino-1,2-benzoquinone 2-oxime

(0.13 g, 1%) 3-acetylamino-1,4-benzoquinone 4-oxime (5.2 g, 43%) (conformed by t.l.c. and comparative i.r. with authentic samples *cf.* 4.4.1) was obtained by concentration of the filtrate.

4.4.28 Reaction of 5-Acetylamino-1,2-benzoquinone 2-oxime with Manganese(II) Chloride Tetrahydrate in Methanol at 20 °C

To a solution of manganese(II) chloride tetrahydrate (1.2 g, 6.1 mmol) in methanol (10 cm^3), a suspension of 5-acetylamino-1,2-benzoquinone 2-oxime (2.2 g, 12 mmol) in methanol (50 cm^3) was added with stirring (96 h). Filtration afforded the unreacted ligand (1.8 g, 82% recovery) (confirmed by comparative t.l.c. with an authentic sample *cf.* 4.4.1).

4.4.29 Reaction of 5-Acetylamino-1,2-benzoquinone 2-oxime with Manganese(II) Chloride Tetrahydrate in Methanol Under Reflux

5-Acetylamino-1,2-benzoquinone 2-oxime (1.9 g, 11 mmol) and manganese(II) chloride tetrahydrate (1.1 g, 5.6 mmol) in methanol (50 cm^3) were heated under reflux (4 h). Filtration gave a brown solid (1.4 g) (multicomponent by t.l.c.).

4.4.30 Reaction of 5-Acetylamino-1,2-benzoquinone 2-oxime with Manganese(II) Chloride Tetrahydrate in Methanol in the presence of ammonium buffer

To a solution of manganese(II) chloride tetrahydrate (0.2 g, 1 mmol) in methanol (20 cm^3), solid 5-acetylamino-1,2-benzoquinone 2-oxime (0.46 g, 2.6 mmol) was added with stirring. This was followed by the addition of ammonium buffer solution (2 cm^3, pH 10) and the mixture was left to stir (12 h). Filtration afforded a green-black solid which was washed with water (3 X 10 cm^3), diethyl ether (6 X 10 cm^3) and dried at 0.1 mm/20 °C to give tris(5-acetylamino-1,2-benzoquinone 2-oximato)manganese(III) monohydrate (confirmed by t.l.c. and comparative i.r. with an authentic sample *cf.* 4.4.27).

4.4.32 Interacion of Tris(5-acetylamino-1,2-benzoquinone 2-oximato)manganese(III) with Pyridine

To a suspension of tris(5-acetylamino-1,2-benzoquinone 2-oximato)manganese(III) (0.5 g, 0.8 mmol) in acetone (50 cm^3), pyridine (1.3 g, 17 mmol) was added with stirring under reflux (10 h). Concentration of the mixture to dryness under nitrogen afforded a green-black solid which was washed with light petroleum (b.p. 30-40 °C) and dried at 0.1 mm/20 °C to give tris(5-acetylamino-1,2-benzoquinone 2-oximato)-manganese(III) (0.5 g, 100% recovery) (identified by

comparative t.l.c. and i.r. with an authentic sample *cf.* 4.4.27).

4.4.32 Reaction of Bis(1,2-naphthoquinone 1-oximato)-nickel(II) with Dimethyl Acetylenedicarboxylate in Ethylene Glycol Dimethyl Ether-Water Mixture

Bis(1,2-naphthoquinone 1-oximato)nickel(II) (1.1 g, 2.6 mmol) and DMAD (2.8 g, 20.0 mmol) in EDGE-water (7.5:1) (85 cm^3) mixture were heated under reflux (24 h). Filtration afforded a brown solid which was washed with methanol (3 x 10 cm^3), water (3 X 10 cm^3) and dried at 0.1 mm/20 °C to give crude nickel(II) butynedioate (0.40 g, 70%), μ_s 3.0 (Found: C, 21.9; H, 2.6; Ni, 28.0; N, 1.3) (confirmed by comparative i.r. with an authentic sample; *cf.* 4.4.34). The residue remaining after removal of the solvent from the filtrate was refluxed in toluene (60 cm^3). On cooling a yellow solid separated which was recrystallised from toluene to give 4-hydroxy-2,3-dimethoxycarbonyl-1,4-naphthoxazine (14) (1.14 g, 70%) m.p. 161-162 °C (lit.[2] m.p. 159-160 °C) (Found: M^+, 315; C, 60.0 ; H, 4.1 ; N, 4.5 . Calc. for $C_{16}H_{13}NO_6$: M^+, 315; C, 61.0; H, 4.1; N, 4.4%).

4.4.33 Reaction of Bis(1,2-naphthoquinone 2-oximato)-nickel(II) with Dimethyl Acetylenedicarboxylate in Ethylene Glycol Dimethyl Ether-Water Mixture

Bis(1,2-naphthoquinone 2-oximato) nickel(II) (1.0 g, 2.5 mmol) and DMAD (1.4 g, 10.0 mmol) in EGDE-water (85t cm^3) (7.5:1) were heated under reflux (24 h). Filtration gave a pink solid which was washed with methanol (3 X 10 cm^3), water (3 X 10 cm^3) and dried at 0.1 mm/20 °C to give crude nickel(II) butynedioate (0.23 g, 44%), μ_B 3.0 (Found: C, 12.9; H, 2.2; Ni, 28.0%) (confirmed by comparative i.r. with an authentic sample; *cf.* 4.4.34) and a dark brown filtrate. Evaporation of the solvent from the filtrate gave a residue (multicomponent by t.l.c.) which was refluxed in toluene (60 cm^3) for 1 h. Filtration afforded a brown solid (1.54 g) and a red filtrate. Concentration and cooling of the filtrate gave yellow crystals of 4-hydroxy-2,3-dimethoxycarbonyl-1,4-naphthoxazine (15), (0.13 g, 8%), m.p. 163-164 °C (lit.[2] m.p. 163-164°C), (Found: M^+, 315; C, 60.1; H, 4.1; N, 4.5. Calc. for $C_{16}H_{13}NO_6$: M^+, 315; C, 60.9; H, 4.1; N, 4.4%). Flash chromatography of the brown solid on silica gel with toluene gave traces of an oily yellow residue. Further elution with toluene-ethyl acetate (9:5) gave more of the cycloadduct (15) (0.3 g, 19%). Subsequent elution with methanol gave a brown solid (multicomponent by t.l.c.) (1.2 g) (Found: Ni, 2.2%).

4.4.34 Reaction of Bis(4-bromo-1,2-benzoquinone 2-oximato)nickel(II) with Dimethyl Acetylenedicarboxylate in Ethylene Glycol Dimethyl Ether -Water Mixture

Bis(4-bromo-1,2-benzoquinone 2-oximato)nickel(II) (1.0 g, 2.2 mmol) and DMAD (1.5 g, 11 mmol) in EGDE-water (85 cm^3) (7.5:1) were heated under reflux (24 h). Filtration gave a pink solid which was washed with methanol (2 X 5 cm^3), water (2 X 5 cm^3) and dried at 0.1 mm/20 °C to give *nickel(II) butynedioate octahydrate* (0.29 g, 42%), μ_B 2.0 (Found: C, 14.5; H, 4.5; Ni, 18.6. $C_4H_{16}NiO_{12}$ requires: C, 15.3; H, 5.1; Ni, 18.8%). Concentration and cooling of the filtrate afforded a yellow solid which was filtered off and recrystallised from acetone-dichloromethane (2:1) to give *6-bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one* (17, R = Br) (0.65g, 48 %), m.p. 178-179 °C (Found: M^+, 297; C, 44.5; H, 2.7; N, 4.8. $C_{11}H_8BrNO_4$ requires: M^+, 297; C, 44.4; H, 2.7; N, 4.7%). Evaporation of the solvent from the filtrate and flash chromatography of the residue over silica gel with dichloromethane afforded more of the benzoxazinone (0.54 g, 40%) (identified by t.l.c. and i.r. *cf.* above). Further elution with ethyl acetate gave an orange oily residue (0.4 g) (multicomponent by t.l.c.) and final elution with methanol afforded a solid (1.0 g) (multicomponent by t.l.c.) (Found: C, 30.2; H, 3.7; N, 1.0; Ni, 1.2%).

In another experiment, DMAD (1.2 g, 8.3 mmol) and bis(4-bromo-1,2-benzoquinone 2-oximato)nickel(II) (1.1 g, 2.4 mmol) were heated under reflux in EGDE-water (80 cm^3) (7.5:1) for 24 h. Filtration of the mixture gave nickel(II) butynedioate octahydrate (0.26 g, 33%) (confirmed by elemental analysis and comparative i.r. with an authentic sample *cf.* above). Evaporation of the solvent form the filtrate and flash chromatography of the resultant residue over silica gel with toluene gave the 1,4-benzoxazinone (17, R = 6-Br) (0.47 g, 35%) (identified by comparative m.p., i.r., m.s., and ^1H n.m.r. with authentic sample *cf.* above). Further elution with toluene-dichloromethane (9:1) afforded 6-bromo-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine (16, R = 6-Br) (0.51 g, 32%), m.p. 214-215 °C (lit.[2] m.p. 196-197 °C) (Found: M^+, 343; C, 41.9; H, 2.9; N, 4.1. Calc. for $C_{12}H_{10}BrNO_6$: M^+, 343; C, 42.0; H, 2.9; N, 4.1%). Elution with ethyl acetate gave a red-brown oil (0.33 g) (multicomponent by t.l.c.). Further elution with methanol gave a solid (1.0 g) (multicomponent by t.l.c.) (Found:Ni, 1.2%).

4.4.35 Reaction of Bis(4-chloro-1,2-benzoquinone 2-oximato)nickel(II) with Dimethyl Acetylenedicarboxylate in Ethylene Glycol Dimethyl Ether -Water Mixture

Bis(4-chloro-1,2-benzoquinone 2-oximato)nickel(II) (1.0 g, 2.8 mmol) and DMAD (1.2 g, 8.5 mmol) in

EGDE-water (7.5:1) (85 cm^3) were heated under reflux (24 h). Filtration gave a pink solid which was washed with methanol (2 X 5 cm^3), water (2 X 5 cm^3) and dried at 0.1 mm/20 °C to give nickel(II) butynedioate octahydrate (0.34 g, 38%), μ_s 2.0 (Found: C, 14.5, H, 2.5; Ni, 18.6. Calc. for $C_4H_{16}NiO_{12}$: C, 15.3; H, 5.1; Ni, 18.8%). Evaporation of the solvent from the filtrate and flash chromatography of the residue with toluene gave *6-chloro-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one* (17, R = Cl), (0.44 g, 30%), m.p. 188-189 °C (Found: M^+, 253; C, 52.2; H, 3.2; N, 5.6. $C_{11}H_8ClNO_4$ requires: C, 52.2; H, 3.2; N, 5.5%). Further elution with toluene-dichloromethane (9:1) afforded 6-chloro-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine (16, R = 4-Cl), (0.42 g, 25%), m.p. 206-207 °C (lit.[2] m.p. 186-188 °C) (Found: M^+, 299; C, 48.2; H, 3.4; N, 4.7. Calc. for $C_{12}H_{10}ClNO_6$: M^+, 299; C, 48.2; H, 3.3; N, 4.7%). Elution with ethyl acetate gave a red-brown oil (0.66 g) (multicomponent by t.l.c.) and final elution with methanol afforded a solid (0.09 g) (multicomponent by t.l.c.) (Found: Ni, 1.21%)

4.4.36 Reaction of Bis(4-methyl-1,2-benzoquinone 2-oximato)nickel(II) with Dimethyl Acetylenedicarboxylate in Ethylene Glycol Dimethyl Ether-Water Mixture

Bis(4-methyl-1,2-benzoquinone 2-oximato)nickel(II) (1.0 g, 3.1 mmol) and DMAD (1.7 g, 1.2 mmol) in

EGDE-water (85 cm^3) (7.5:1) were heated under reflux (24 h). Filtration gave a pink solid which was washed with methanol (2 X 10 cm^3), water (2 X 10 cm^3) and dried at 0.1 mm/20 °C to give crude nickel(II) butynedioate (0.42 g, 66%), μ_B 2.9 (Found: C, 21.7; H, 3.1, Ni, 28.0; N, 1.5) (confirmed by comparative i.r. with an authentic sample; *cf.* 4.4.34). The filtrate on concentration afforded a yellow solid which was filtered off and recrystallised from toluene to give 6-methyl-2,3-dimethoxycarbonyl-1,4-benzoxazine (16, R = 6-Me), (0.14 g, 10%), m.p. 188-190 °C (lit.[2] m.p. 186-187 °C) (Found: M^+, 279; C, 55.8; H, 4.7; N, 5.0. Calc. for $C_{13}H_{13}NO_6$: M^+, 279; C, 55.9; H, 4.7; N, 5.0%). The solvent was evaporated from the filtrate and the residue was flash chromatographed on silica gel. Elution with toluene gave *6-methyl-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one* (17, R = 6-Me), (0.29 g, 20%), m.p. 144-145 °C (Found: M^+, 233; C, 61.8; H, 4.9; N, 5.45. $C_{13}H_{11}NO_4$ requires: M^+, 233; C, 61.8; H, 4.7; N, 6.0%). Further elution with toluene-dichloromethane (9:1) gave more of the 1,4-benzoxazine (0.96 g, 55%) (identified by i.r. and t.l.c.; *cf.* above). Elution with ethyl acetate gave an oily orange-brown substance (0.11 g) (multicomponent by t.l.c.) and final elution with methanol afforded a solid (0.22 g) (multicomponent by t.l.c.) (Found: Ni, 5.9%).

4.4.37 Reaction of Bis(1,2-naphthoquinone 1-oximato)-copper(II) with Dimethyl Acetylenedicarboxylate in Ethylene Glycol Dimethyl Ether-Water Mixture

Bis(1,2-naphthoquinone 1-oximato)copper(II) (1.0 g, 2.5 mmol) and DMAD (1.4 g, 9.8 mmol) in EGDE-water (85 cm^3) (7.5:1) were heated under reflux (3 h). Filtration gave a brown solid which was washed with methanol (3 X 10 cm^3), water (3 X 10 cm^3) and dried at 0.1 mm/20 °C to give crude copper(II) butynedioate (0.39, 90%), μ_B 2.4 (Found: C, 15.7; H, 1.1; Cu, 36.0; N, 0.5) (confirmed by comparative i.r. with an authentic sample *cf.* 4.4.34). Evaporation of the solvent from the filtrate gave a residue (multicomponent by t.l.c.) which was mixed with silica gel. Flash chromatography with toluene-ethyl acetate (9:1) afforded 4-hydroxy-2,3-dimethoxycarbonyl-1,4-naphthoxazine (14) (1.1 g, 70%), m.p. 153-155 °C (lit.[2] m.p. 159 - 160 °C (Found: M^+, 315; C, 60.5; H, 4.2; N, 4.4. Calc. for $C_{16}H_{13}NO_6$: C,60.9; H,4.1; N, 4.4%).

4.4.38 Reaction of Bis(1,2-naphthoquinone 2-oximato)-copper(II) with Dimethyl Acetylenedicarboxylate in Ethylene Glycol Dimethyl Ether-Water Mixture

Bis(1,2-naphthoquinone 2-oximato)copper(II) (1.0 g, 2.5 mmol) and DMAD (1.5 g, 10.7 mmol) in EGDE-water

(85 cm^3) (7.5:1.0) were heated under reflux for 3 h. Filtration gave a brown solid which was washed with methanol (3 X 10 cm^3), water (3 X 10 cm^3) and dried at 0.1 mm/20 °C to give crude hydrated copper(II) butynedioate (0.40 g, 92%), μ_B 2.4 (Found: C, 17.2; H, 1.1; Cu, 36.0; N, 0.6) (confirmed by comparative i.r. with an authentic sample; *cf.* 4.4.34). Evaporation of the solvent from the filtrate and flash chromatography of the residue on silica gel with toluene gave an orange oily residue (0.32 g) (multicomponent by t.l.c.). Further elution with toluene-dichloromethane (8:2) gave 4-hydroxy-2,3-dimethoxycarbonyl-1,4-naphthoxazine (15) (0.6 g, 38 %), m.p. 163-164 °C (lit.[2] m.p. 163-164 °C) (Found: M^+, 315; C, 60.7; H, 4.2; N, 4.4. Calc. for $C_{16}H_{13}NO_6$: M^+, 315; C, 61.0; H, 4.1; N, 4.4%).

4.4.39 Reaction of Bis(4-R-1.2-benzoquinone 2-oximato)-copper(II) (R = Br, Cl, Me) with Dimethyl Acetylenedicarboxylate in Ethylene Glycol Dimethyl Ether-Water Mixture

The copper complex (1 mol equiv.) and DMAD (4 mol equiv.) in EGDE-water (85 cm^3) (7.5:1) were heated under reflux (24 h). Filtration afforded a paramagnetic brown-green solid which was washed with methanol (3 X 10 cm^3) and water (3 X 10 cm^3) and dried at 0.1 mm/20 °C to give crude copper(II) butynedioate (see Table 4.1 for results; confirmed by comparative i.r. with an authentic sample *cf.* 4.4.34). Evaporation of the

solvent from the filtrate afforded a residue which was mixed with silica gel and flash chromatographed. Elution with toluene afforded the 1,4-benzoxazinone (17) followed by the corresponding 1,4-benzoxazine (16) which was eluted with toluene-dichloromethane (9:1) (see Table 4.2 for yields and other data; confirmed by comparative i.r., m.p., m.s., and ^{1}H n.m.r. with authentic samples; *cf.* 4.4.34, 4.4.35, 4.4.36). Further elution with dichloromethane-ethyl acetate (1:1) gave an oily residue (multicomponent by t.l.c.) and subsequent elution with methanol afforded a brown solid (multicomponent by t.l.c.).

Table 4.1 Yield and Elemental Analysis for $Cu(bd).nH_2O$ Obtained from the $Cu(4\text{-}Rqo)_2$/DMAD Systems

$Cu(4\text{-}Rqo)_2$		Product						
		$Cu(bd).nH_2O$[a]						
		Yield		Found (%)				μ_B
R	(g)	(g)	(%)[b]	C	H	Cu	N	
4-Br	1.08	0.38	87	17.5	0.9	33.6	0.6	1.6
4-Cl	1.03	0.34	62	17.7	0.9	33.6	0.5	2.0
4-Me	1.02	0.36	67	21.2	1.5	36.0	1.8	2.3

a=Calc. for $Cu(bd).H_2O$: C, 24.7; H, 1.0; Cu, 33.0%
Calc. for $Cu(bd).4H_2O$: C, 19.4; H, 3.22; Cu, 25.8%
b=Based on copper content

Table 4.2 Yields and other Data for the Organic Products Obtained from the $Cu(4\text{-}Rqo)_2$/DMAD Systems

$Cu(4\text{-}Rqo)_2$		Product								
		1,4-Benzoxazine[a]		1,4-Benzoxazinone						
R	(g)	Yield		Yield		M.p. (°C)	Found (%) [Required]			
		(g)	(%)	(g)	(%)		C	H	N	M⁺
4-Br	1.08	0.86	54	0.14	11	178 - 179	44.5 44.4	2.7 2.7	4.8 4.7	297
4-Cl	1.03	0.56	32	0.39	27	188 - 189	52.2 52.2	3.18 3.16	5.6 5.5	253
4-Me	1.02	1.28	75	0.02	1.4	189 - 190	61.8 61.8	4.9 4.7	5.5 6.0	233

a=Satisfactory elemental analysis (confirmed by comparative m.s. and ^1H n.m.r.)

4.4.40 Reaction of Bis(5-acetylamino 1,2-benzoquinone 2-oximato)copper(II) with Dimethyl Acetylenedicaboxylate in Ethylene Glycol Dimethyl Ether-Water Mixture

Bis(5-acetylamino-1,2-benzoquinone 2-oximato)copper(II) (1.1 g, 2.5 mmol) and DMAD (1.4 g, 10 mmol) in EGDE-water (85 cm^3) (7.5:1.0) mixture were heated under reflux (9 h). Filtration gave crude copper(II) butynedioate (0.37 g, 88%), μ_B 2.3 (Found: C, 18.6; H, 1.5; Cu, 36.0; N, 2.4 %) (confirmed by comparative i.r. with authentic sample; cf 4.4.34) and a red-brown filtrate. The filtrate was chromatographed on silica gel. Elution with toluene-ethyl acetate (7:3) gave 7-acetylamino-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine (1.3 g, 76%), m.p 190-191 °C (Found: M^+, 322; C, 52.2; H, 4.6; N, 8.6. $C_{14}H_{14}N_2O_7$ requires: M^+, 322; C, 52.1; H, 4.3; N, 8.7 %). Further elution with ethyl acetate gave a red eluate which on concentration gave an unidentified red solid (0.15 g) (single component by t.l.c.) m.p. 255 °C (decomp.) (Found: M^+, 279; C, 56.5; H, 5.3; N, 5.3%). Elution with methanol gave a brown solid (0.1 g) (multicomponent by t.l.c.) (Found: Cu, 18.9%).

4.4.41 Reaction of Tris(1,2-naphthoquinone 1-oximato)-cobaltate(III) with Dimethyl acetylenedicarboxylate in Toluene

Tris(1,2-naphthoquinone 1-oximato)cobalt(III) (0.5 g,

0.9 mmol) and DMAD (0.9 g, 6.0 mmol) in toluene (50 cm^3) were heated under reflux (48 h). Filtration gave unreacted complex (0.45 g, 85% recovery) (identified by i.r.).

4.4.42 Reaction of Tris(1,2-naphthoquinone 1-oximato)-cobaltate(III) with Dimethyl acetylenedicarboxylate in Ethylene Glycol Dimethyl-Water Mixture

Tris(1,2-naphthoquinone 1-oximato)cobalt(III) (0.5 g, 0.9 mmol) and DMAD (0.9 g, 6.0 mmol) in EGDE-water (7.5:1) (85 cm^3) mixture were heated under reflux (48 h). Filtration gave unreacted complex (0.42 g, 82% recovery) (identified by i.r.).

4.4.43 Reaction of Bis(1,2-naphthoquinone 1-oximato)-copper(II) with Methyl Propiolate in Ethylene Glycol Dimethyl Ether-Water Mixture

Bis(1,2-naphthoquinone 1-oximato)copper(II) (1.1 g, 2.5 mmol) and MP (0.86 g,10.0 mmol) in EGDE-water (7.5:1) (85 cm^3) were heated under reflux (18 h). Filtration gave crude copper(II) propynoate (0.33 g, 78%) (Found: C, 39.2; H, 2.3; Cu, 36.7; N, 1.7%) and a brown filtrate. The residue remaining after removal of the solvent from the filtrate was mixed with silica gel and flash chromatographed. Elution with toluene gave traces of an oily brown residue (0.08 g) (multicomponent

by t.l.c.) followed by 1,3-naphthoxazole-2-carboxylate (22) (0.13 g, 12%) (confirmed by comparative i.r. and m.s. with an authentic sample; *cf.* 4.4.47). Further elution with toluene-dichloromethane (9:1) afforded yellow *4-hydroxy-monomethoxycarbonyl-1,4-naphthoxazine* (0.82 g, 65%), m.p. 159-160 °C (Found: M^+, 257; C, 66.5; H, 4.4; N, 5.4. $C_{14}H_{11}NO_4$ requires : M^+, 257; C, 65.4; H, 4.3; N, 5.4%). Subsequent elution with methanol gave a brown solid (0.35 g) (multicomponent by t.l.c.) (Found: Cu, 7.8 %).

4.4.44 Reaction of Bis(5-acetylamino-1,2-benzoquinone-2-oximato)copper(II) with Methyl Propiolate in Ethylene Glycol Dimethyl Ether-Water Mixture

Bis(5-acetylamino-1,2-benzoquinone 2-oximato)copper(II) (1.1 g, 2.6 mmol) and MP (0.85 g, 10.0 mmol) in EGDE-water (7.5:1.0) (85 cm^3) mixture were heated under reflux (18 h). Filtration gave black bis(5-acetylamino-1,2-benzoquinone 2-oximato)copper(II) (0.8 g, 73% recovery) (Found: C, 45.2; H, 3.3; Cu, 14.9; N, 13.1. Calc. for $C_{16}H_{14}CuNO_6$: C, 45.6; H, 3.3; Cu, 15.2; N, 13.3%). Evaporation of the solvent from the filtrate gave a multicomponent oily residue which which could not be separated by chromatography.

4.4.45 Reaction of Bis(1,2-naphthoquinone 1-oximato)-nickel(II) with Methyl Propiolate in Ethylene Glycol Dimethyl Ether-Water Mixture

Bis(1,2-naphthoquinone 1-oximato)nickel(II) (1.0 g, 2.5 mmol) and MP (0.85 g, 10 mmol) in EGDE-water (7.5:1) (85 cm^3) mixture were heated under reflux (18 h). Filtration gave a brown filtrate and the unreacted complex (0.64 g, 64%) (identified by i.r.). The residue remaining after removal of the solvent was refluxed in toluene 100 cm^3). On cooling 4-hydroxy-monomethoxycarbonyl-1,4-naphthoxazine (0.30 g, 23%), m.p. 159-160 °C (Found: M^+, 257; C, 65.5; H, 4.4; N, 5.4. Calc. for $C_{14}H_{11}NO_4$: M, 257; C, 65.4; H, 4.3; N, 5.4%) was filtered off and dried in air..

In another experiment bis(1,2-naphthoquinone 1-oximato)nickel(II) (1.1 g, 2.5 mmol) and MP (1.7 g, 21 mmol) in EGDE-water (7.5 : 1.0) (85 cm^3) mixture were heated under reflux (72 h). Filtration gave a brown filtrate and the unreacted complex (0.59 g, 54% recovery) (identified by i.r.). The residue remaining after removal of the solvent was refluxed in toluene 100 cm^3). On cooling 4-hydroxy monomethoxycarbonyl-1,4-naphthoxazine (0.40 g, 29.0%) m.p. 159-160 °C. (confirmed by t.l.c. and comparative i.r. with an authentic sample; *cf* above) was filtered off and dried in air.

4.4.46 Reaction of Bis(5-acetylamino-1,2-benzoquinone-2-oximato)nickel(II) with Methyl Propiolate in Ethylene Glycol Dimethyl Ether-Water Mixture

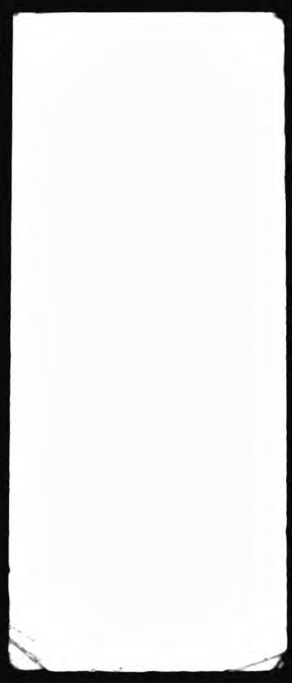
Bis(5-acetylamino-1,2-benzoquinone 2-oximato)nickel(II) (1.1 g, 2.6 mmol) and MP (0.85 g, 10 mmol) in EGDE-water mixture (7.5:1) (85 cm^3) mixture were heated under reflux (18 h). Filtration gave the unreacted complex (95%, recovery) (identified by i.r.).

4.4.47 Aerobic Oxidation of 4-Hydroxy-monomethoxycarbonyl-1,4-naphthoxazine in the Presence of Bis(1,2-naphthoquinone 1-oximato)copper(II)

4-Hydroxy-monomethoxycarbonyl-1,4-naphthoxazine (0.1 g, 0.6 mmol) was heated under reflux in methanol (25 cm^3) in the presence of bis(1,2-naphthoquinone 1-oximato)copper(II) (0.009 g, 0.02 mmol). After 20 h the mixture was filtered. The filtrate was chromatographed on silica. Elution with toluene-ethyl acetate (2:1) gave methyl-1,3-naphthoxazole 2-carboxylate (22) (0.13 g, 94%) m.p. 141-142°C (lit.[3] m.p. 140-141 °C) (Found: M^+, 227 C, 68.7; H,4.0; N, 6.2. Calc. for $C_{13}H_9NO_3$: M^+, 227; C, 68.7; H, 4.0; N, 6.1%).

4.4.48 Reaction of Hydrated Metal(II) Butynedioates with Pyridine

Hydrated metal(II) butynedioates were stirred in



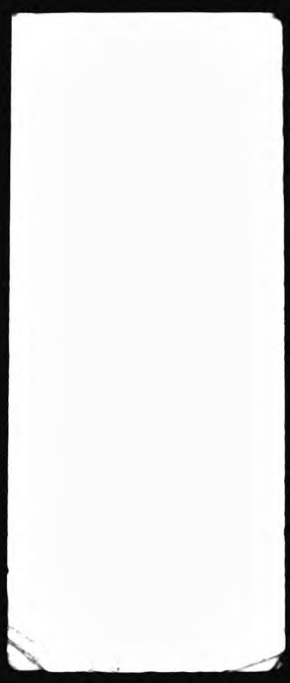
pyridine (20 cm^3) at room temperature (24 h). Filtration afforded a solid which was washed with light petroleum (30-40 °C) and dried at 0.1 mm/20 °C to give the corresponding adduct (see Table 4.3 for results).

Table 4.3 Results Obtained from the Reaction of Metal(II) Butynedioates with Pyridine

Reactant	(g)	Product	(g)	Found (%) [Required] C	H	M	N	μ_B
Ni(bd).nH_2O†	0.23	Ni(bd)(py).$2H_2O$	0.19	39.6	3.2	19.9	6.9	2.83
				37.8	3.1	20.6	4.9	
Ni(bd).nH_2O††	0.18	Ni(bd)(py). H_2O	0.21	40.8	2.9	21.8	7.1	2.86
				40.3	2.6	22.0	5.2	
Cu((bd).nH_2O	0.31	Not Formulated	0.38	36.6	2.3	24.8	6.3	2.21

† Solid isolated from Ni(1-nqo)/DMAD system

†† Solid isolated from Ni(2-nqo)/DMAD system



4.5 References

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APPENDIX I

Details of the Crystal Structure of 3-Acetylamino-1,4-benzoquinone 4-Oxime

Table 1 Fractional Atomic Coordinates and Thermal Parameters [$Å^2$] for the Non-Hydrogen Atoms in 3-Acetylamino-1,4-benzoquinone 4-oxime

Atom	X	Y	Z	U_{eq}
C(1)	0.1526(3)	0.9220(5)	-0.1413(15)	0.032(2)
C(2)	0.0790(4)	0.8820(5)	-0.3180(19)	0.041(2)
C(3)	0.0735(4)	0.7818(5)	-0.4188(18)	0.041(2)
C(4)	0.1403(4)	0.7099(5)	-0.3548(18)	0.041(2)
C(5)	0.2141(4)	0.7504(5)	-0.1836(17)	0.038(2)
C(6)	0.2215(3)	0.8508(4)	-0.0864(16)	0.031(2)
C(7)	0.3572(3)	0.8486(5)	0.2245(17)	0.033(2)
C(8)	0.4219(4)	0.9177(5)	0.3821(20)	0.045(2)
N(1)	0.2915(3)	0.8981(4)	0.0764(15)	0.033(3)
N(2)	0.1628(3)	1.0169(4)	-0.0215(50)	0.042(3)
O(1)	0.1332(2)	0.6175(3)	-0.4464(13)	0.060(3)
O(2)	0.0953(3)	1.0783(4)	-0.0736(15)	0.057(3)
O(3)	0.3630(2)	0.7529(3)	0.2235(14)	0.056(3)

Table 2 Fractional Atomic Coordinates for the Hydrogen Atoms of 3-Acetylamino-1,4-benzoquinone 4-oxime

Atom	X	Y	Z
H(N1)	0.2691	0.9560	0.0544
H(O1)	0.0759	1.1020	0.0905
H(C2)	0.0415	0.9298	-0.3352
H(C3)	0.0206	0.7631	-0.5386
H(C5)	0.2593	0.7060	-0.1288
H1(C8)	0.4521	0.8733	0.5620
H2(C8)	0.4581	0.9504	0.2347
H3(C8)	0.4032	0.9670	0.5279

Table 3 Bond Lengths(Å) for 3-Acetylamino-1,4-benzoquinone 4-oxime

C(1) - C(2)	1.448(7)
C(2) - C(3)	1.338(8)
C(3) - C(4)	1.448(8)
C(4) - C(5)	1.445(8)
C(5) - C(6)	1.337(8)
C(6) - C(1)	1.467(7)
C(6) - N(1)	1.414(7)
C(1) - N(2)	1.301(7)
N(2) - O(2)	1.372(6)
C(7) - N(1)	1.351(7)
C(7) - O(3)	1.224(6)
C(7) - C(8)	1.485(8)
C(4) - O(1)	1.232(7)

Table 4 Bond Angles (°) for 3-Acetylamino-1.4-benzoquinone 4-oxime

C(7) - N(1) - C(6)	126.8(5)
C(2) - C(1) - N(2)	125.2(6)
C(6) - C(1) - C(2)	118.3(5)
C(4) - C(3) - C(2)	121.4(6)
C(5) - C(4) - O(1)	122.1(6)
C(6) - C(5) - C(4)	121.8(6)
C(5) - C(6) - N(1)	126.0(6)
N(1) - C(7) - O(3)	121.7(6)
C(8) - C(7) -N(1)	115.7(5)
C(1) - N(2) - O(2)	113.3(5)
C(6) - C(1) - N(2)	116.5(5)
C(3) - C(2) - C(1)	120.6(6)
C(3) - C(4) - O(1)	120.1(6)
C(5) - C(4) - C(3)	117.8(6)
C(1) - C(6) - N(1)	114.1(5)
C(5) - C(6) - C(1)	119.9(6)
C(8) - C(7) - O(3)	122.6(6)

Table 5 Intermolecular Distances (Å) for 3-Acetylamino-1,4-benzoquinone 4-oxime

Atom(1)	Atom(2)	Distance	S	a	b	c
N(1)	....O(1)	3.12	2	0.0	0.0	-1.0
C(8)	....O(1)	3.15	2	0.0	0.0	-1.0
Hn(1)	....O(1)	2.68	2	0.0	0.0	-1.0
H2(C8)	....O(1)	2.80	2	0.0	0.0	-1.0
H3(C8)	....O(1)	2.61	2	0.0	0.0	0.0
C(2)	....O(2)	3.41	-1	0.0	2.0	0.0
H(2)	....O(2)	2.87	-1	0.0	2.0	0.0
O(3)	....O(2)	2.67	2	0.0	-1.0	0.0
N(2)	....O(3)	3.26	2	0.0	0.0	0.0
Ho(2)	....O(3)	2.27	2	0.0	0.0	0.0
H(3)	....O(3)	2.89	-2	0.0	0.0	0.0
Ho(2)	....C(2)	2.79	-1	0.0	2.0	0.0
H2(C8)	....C(8)	2.92	-1	1.0	2.0	1.0

Symmetry transformations: The second atom is related to the first atom, at (x, y, z) by the symmetry operation S with (a, b, c) added to the (x′, y′, z′) of S.
where S = 1/2

Table 6 Interamolecular Distances (Å) for 3-Acetylamino-1,4-benzoquinone 4-oxime

C(3) ....O(1)	2.33	C(5) ....O(1)	2.34
H(3) ....O(1)	2.64	H(5) ....O(1)	2.60
C(1) ....O(2)	2.23	C(2) ....O(2)	2.68
H(2) ....O(2)	2.29	N(1) ....O(3)	2.25
C(5) ....O(3)	2.83	C(6) ....O(3)	2.85
C(8) ....O(3)	2.38	H(5) ....O(3)	2.19
H1(C8)....O(3)	2.44	H2(C8)....O(3)	2.97
N(2) ....N(1)	2.63	C(1) ....N(1)	2.42
C(5) ....N(1)	2.45	C(8) ....N(1)	2.40
H(5) ....N(1)	2.62	H2(C8)....N(1)	2.87
H3(C8)....N(1)	2.60	C(2) ....N(2)	2.44
C(6) ....N(2)	2.35	Hn(1)....N(2)	1.93
Ho(2)....N(2)	1.88	H(2) ....N(2)	2.53
C(3) ....C(1)	2.42	C(4) ....C(1)	2.83
C(5) ....C(1)	2.43	Hn(1)....C(1)	2.07
Ho(2)....C(1)	2.81	H(2) ....C(1)	1.94
C(4) ....C(2)	2.43	C(5) ....C(2)	2.82
C(6) ....C(2)	2.50	H(3) ....C(2)	1.96
C(5) ....C(3)	2.48	C(6) ....C(3)	2.83
H(2) ....C(3)	1.99	C(6) ....C(4)	2.43
H(3) ....C(4)	2.17	H(5) ....C(4)	2.10
C(7) ....C(5)	3.02	Hn(1)....C(5)	2.90
C(7) ....C(6)	2.47	Hn(1)....C(6)	1.63
H(5) ....C(6)	1.96	Hn(1)....C(7)	2.08
H(5) ....C(7)	2.73	H1(C8)....C(7)	1.99

Table 7 Anisotropic Temperature Coefficients ($Å^2$) for 3-Acetylamino-1,4-benzoquinone 4-oxime

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	0.033(3)	0.036(3)	0.030(3)	0.01(3)	-0.005(2)	0.001(3)
N(2)	0.042(3)	0.040(3)	0.044(4)	0.06(3)	0.011(3)	0.002(3)
O(1)	0.071(3)	0.044(3)	0.065(4)	-0.03(2)	0.006(3)	-0.014(3)
O(2)	0.038(2)	0.050(3)	0.083(4)	0.08(2)	-0.002(3)	-0.009(3)
O(3)	0.057(3)	0.040(2)	0.072(3)	0.06(2)	-0.003(3)	0.005(3)

Observed and Calculated Structure Facors for 3-Acetylamino-1,4-benzoquinone 4-oxime

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
4	0	0	1052	-1050	6	3	0	456	-456	1	7	0	107	-111	2	11	0	158	165
6	0	0	123	-131	7	3	0	514	514	2	7	0	79	-78	3	11	0	77	-74
8	0	0	84	81	8	3	0	465	457	5	7	0	177	184	4	11	0	172	178
10	0	0	117	-127	9	3	0	120	-119	7	7	0	83	-88	6	11	0	210	-217
14	0	0	401	386	10	3	0	123	125	8	7	0	72	-74	7	11	0	168	186
16	0	0	164	-168	11	3	0	104	-103	10	7	0	59	62	0	12	0	103	103
18	0	0	76	-73	12	3	0	113	-111	0	8	0	301	297	1	12	0	77	-91
3	1	0	62	-63	14	3	0	65	-40	2	8	0	161	-157	2	12	0	51	-66
5	1	0	76	-88	0	4	0	228	-240	4	8	0	71	-61	5	12	0	93	86
6	1	0	230	219	2	4	0	48	-43	5	8	0	90	-91	9	12	0	88	-90
8	1	0	91	-93	3	4	0	116	-122	6	8	0	80	75	2	13	0	142	-137
9	1	0	115	-124	5	4	0	45	-19	7	8	0	127	-125	3	13	0	71	-72
11	1	0	177	175	6	4	0	241	242	8	8	0	66	54	1	14	0	53	62
12	1	0	124	-120	7	4	0	123	122	9	8	0	152	166	-17	0	1	73	73
13	1	0	110	116	9	4	0	66	66	11	8	0	71	74	-15	0	1	270	-278
15	1	0	185	-176	10	4	0	107	-118	12	8	0	98	-104	-11	0	1	198	192
19	1	0	56	48	13	4	0	64	-68	14	8	0	76	93	-9	0	1	91	88
0	2	0	219	-210	1	5	0	51	38	2	9	0	66	-69	-7	0	1	53	-59
1	2	0	494	503	2	5	0	292	-285	3	9	0	135	134	-5	0	1	168	-165
2	2	0	155	156	3	5	0	93	-100	4	9	0	132	125	-3	0	1	93	-81
3	2	0	138	-141	4	5	0	107	-111	5	9	0	68	-77	-1	0	1	257	-255
5	2	0	383	379	5	5	0	225	221	6	9	0	219	218	1	0	1	266	266
7	2	0	182	182	6	5	0	122	134	7	9	0	59	-49	5	0	1	195	177
8	2	0	203	-198	7	5	0	124	-117	8	9	0	369	-352	7	0	1	161	-162
9	2	0	170	-168	8	5	0	132	129	9	9	0	127	-126	9	0	1	158	-161
10	2	0	84	82	15	5	0	69	53	11	9	0	101	96	11	0	1	113	104
11	2	0	89	-91	0	6	0	575	-611	12	9	0	81	91	13	0	1	136	118
12	2	0	194	202	1	6	0	210	-206	1	10	0	69	-82	15	0	1	126	-122
13	2	0	139	-134	2	6	0	65	-69	2	10	0	61	65	-17	1	1	163	184
14	2	0	147	-162	3	6	0	141	138	4	10	0	56	-49	-16	1	1	159	-164
15	2	0	170	174	4	6	0	217	218	5	10	0	196	198	-15	1	1	138	-148
16	2	0	79	-62	6	6	0	180	179	7	10	0	83	-81	-13	1	1	83	-92
1	3	0	230	221	7	6	0	50	-50	8	10	0	87	-81	-11	1	1	124	112
2	3	0	192	-203	10	6	0	119	-103	9	10	0	161	-142	-9	1	1	55	-54
3	3	0	555	-555	14	6	0	89	-98	11	10	0	59	53	-8	1	1	211	209
4	3	0	179	-190	15	6	0	85	-85	12	10	0	67	67	-7	1	1	162	-160

H	K	L	10FO	10FC
7	2	1	118	106
8	2	1	290	287
10	2	1	118	125
12	2	1	189	-196
13	2	1	119	133
-12	3	1	103	120
-11	3	1	69	-63
-9	3	1	64	63
-8	3	1	271	-256
-7	3	1	93	-88
-6	3	1	115	90
-5	3	1	74	-70
-3	3	1	253	266
-2	3	1	269	269
-1	3	1	55	56
0	3	1	50	-54
1	3	1	91	-92
3	3	1	453	-484
7	3	1	255	269
8	3	1	66	-54
9	3	1	129	134
12	3	1	209	210
13	3	1	129	-139
14	3	1	84	-75
-16	4	1	60	-39
-12	4	1	76	86
-11	4	1	61	-52
-10	4	1	262	250
-9	4	1	59	51
-8	4	1	249	-245
-6	4	1	188	-189
-3	4	1	51	-62
-2	4	1	154	160
3	4	1	474	-474
4	4	1	274	271
5	4	1	193	204
6	4	1	268	-269
7	4	1	178	182
9	4	1	84	-81
10	4	1	59	72
15	4	1	64	45
-16	5	1	66	63
-12	5	1	85	66
-10	5	1	129	-138
-9	5	1	93	-97
-8	5	1	104	-109
-7	5	1	58	-54
-6	5	1	109	108
-5	5	1	83	71
-4	5	1	46	57
-3	5	1	152	143
-2	5	1	291	271
0	5	1	227	-226
1	5	1	187	-177
2	5	1	143	-157
5	5	1	160	-144
6	5	1	90	83
9	5	1	102	119
10	5	1	62	-60
11	5	1	89	79
12	5	1	95	110
14	5	1	73	-73
15	5	1	69	-71
-11	6	1	103	-102
-6	6	1	93	-99
-5	6	1	163	174
-3	6	1	67	-73
-2	6	1	163	166
0	6	1	55	50
1	6	1	77	-77
2	6	1	118	-108
3	6	1	129	-120
5	6	1	222	230
11	6	1	61	-51
-10	7	1	124	-119
-8	7	1	99	-102
-4	7	1	165	169
-3	7	1	349	-340
-1	7	1	235	224
0	7	1	102	96
1	7	1	113	112
2	7	1	59	-57
4	7	1	55	-54
7	7	1	142	-148
9	7	1	70	64
11	7	1	62	-73
13	7	1	77	58
-10	8	1	104	-120
-9	8	1	99	87
-8	8	1	207	200
-6	8	1	95	-90
-4	8	1	101	-104
-3	8	1	112	97
-2	8	1	73	74
-1	8	1	99	-98
0	8	1	51	-48
1	8	1	170	-160
5	8	1	302	301
6	8	1	199	204
8	8	1	235	-223
9	8	1	168	-158
12	8	1	72	84
-12	9	1	110	-102
-9	9	1	60	-41
-8	9	1	145	145
-7	9	1	110	110
-5	9	1	104	-107
-4	9	1	122	-128
-2	9	1	230	
-1	9	1		
2	9	1		
3	9	1		
5	9	1		
6	9	1		
9	9	1		
10	9	1		
11	9	1		
-12	10	1		
-11	10	1		
-10	10	1		
-9	10	1		
-8	10	1		
-7	10	1		
-6	10	1		
-5	10	1		
-3	10	1		
-2	10	1		
-1	10	1		
2	10	1		
3	10	1		
5	10	1		
7	10	1		
-9	11	1		
-7	11	1		
-3	11	1		
-1	11	1		
1	11	1		
3	11	1		
5	11	1		
9	11	1		
-6	12	1		
-5	12	1		
-1	12	1		

H	K	L	10FO	10FC
12	1	2	71	-74
13	1	2	70	62
-11	2	2	128	152
-7	2	2	223	-215
-6	2	2	218	214
-5	2	2	449	-439
-4	2	2	210	-207
-3	2	2	557	528
-2	2	2	303	-283
-1	2	2	138	132
0	2	2	316	318
1	2	2	71	-69
4	2	2	153	-150
5	2	2	86	-80
7	2	2	96	-89
8	2	2	121	124
9	2	2	138	-141
10	2	2	102	-94
11	2	2	255	252
-12	3	2	72	-69
-11	3	2	122	128
-10	3	2	65	80
-6	3	2	90	-83
-4	3	2	213	196
-3	3	2	110	-126
-2	3	2	81	86
-1	3	2	66	62
2	3	2	256	-257
3	3	2	59	43
4	3	2	54	34
6	3	2	55	-50
9	3	2	118	-115
10	3	2	222	227
12	3	2	72	-89
14	3	2	73	-62
-13	4	2	81	58
-12	4	2	131	147
-8	4	2	125	-128
-6	4	2	83	82
-5	4	2	86	-85
-4	4	2	99	-91
-3	4	2	86	89
-2	4	2	114	107
-1	4	2	127	134
0	4	2	110	-112
2	4	2	135	130
3	4	2	77	-67
5	4	2	118	-118
9	4	2	79	84
10	4	2	92	-90
11	4	2	70	49
12	4	2	129	161
-13	5	2	93	108
-11	5	2	103	-94
-9	5	2	73	-68
-6	5	2	59	-44
-4	5	2	91	-94
-2	5	2	99	105
-1	5	2	167	167
1	5	2	121	136
2	5	2	106	-102
3	5	2	304	-301
4	5	2	134	128
7	5	2	70	80
-6	6	2	63	48
-5	6	2	73	76
-4	6	2	93	-106
-3	6	2	163	-160
-2	6	2	67	-37
0	6	2	69	71
2	6	2	96	-110
3	6	2	95	91
4	6	2	86	99
6	6	2	80	64
7	6	2	101	-128
10	6	2	92	-86
-11	7	2	118	-105
-8	7	2	136	112
-7	7	2	64	37
-6	7	2	93	-105
-3	7	2	73	72
0	7	2	80	-87
1	7	2	71	-84
3	7	2	227	-216
5	7	2	207	210
6	7	2	179	166
7	7	2	76	69
8	7	2	131	-124
10	7	2	66	-33
-11	8	2	109	-94
-10	8	2	99	-89
-7	8	2	204	204
-4	8	2	94	81
-3	8	2	91	-79
1	8	2	106	-102
3	8	2	97	-104
4	8	2	65	-50
5	8	2	138	136
6	8	2	163	138
7	8	2	83	83
-10	9	2	133	-152
-9	9	2	157	-162
-6	9	2	141	136
-5	9	2	132	127
-4	9	2	76	-81
1	9	2	73	-78
2	9	2	141	154
4	9	2	88	-90
5	9	2	93	82
9	9	2	72	50
0	10	2	68	67
2	10	2	104	-99
4	10	2	213	208
5	10	2	243	-242
6	10	2	111	120
-4	11	2	104	-103
-3	11	2	102	99
0	11	2	79	-52
2	11	2	138	119
3	11	2	139	-138
-2	12	2	96	103
2	12	2	108	89
-9	0	3	97	-95
-7	0	3	67	-50
-5	0	3	117	-123
-3	0	3	173	167
-1	0	3	88	-74
1	0	3	125	137
3	0	3	78	-100
5	0	3	115	108
-7	1	3	79	-62
-6	1	3	101	105
-3	1	3	87	68
0	1	3	106	98
1	1	3	105	106
2	1	3	147	-147
7	1	3	174	-169
8	1	3	110	95
9	1	3	90	81
-10	2	3	72	-60
-7	2	3	115	-115
-5	2	3	89	77
-4	2	3	127	-118
-3	2	3	96	-79
1	2	3	88	-90

H	K	L	10FO	10FC
4	7	3	137	-131
6	7	3	92	95

H	K	L	10FO	10FC
0	8	3	113	-111
2	8	3	96	111

H	K	L	10FO	10FC
5	8	3	90	-74
-3	9	3	73	-53

H	K	L	1
-1	9	3	

K	L	10FO	10FC
9	3	97	121

H	K	L	10FO	10FC
-4	3	4	85	-89

APPENDIX II

Details of the Crystal Structure of 6-Bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one

Table 1 Atomic Coordinates and Thermal Parameters ($Å^2$) for the Non-Hydrogen Atoms in 6-Bromo-3,4-dihydro--3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxzin-2-one

Atom	x	y	z	U_{eq}
Br	1.0619(1)	0.0930(4)	0.1068(1)	0.044(1)
C(1)	0.9406(8)	0.2643(32)	0.1307(6)	0.029(3)
C(2)	0.8926(7)	0.4583(31)	0.0790(6)	0.029(3)
C(3)	0.8053(7)	0.5891(34)	0.0989(6)	0.027(3)
C(4)	0.7703(8)	0.5247(27)	0.1680(6)	0.025(3)
C(5)	0.8172(8)	0.3322(30)	0.2178(7)	0.035(4)
C(6)	0.9031(8)	0.2025(32)	0.1980(7)	0.037(4)
C(9)	0.6208(8)	1.1322(33)	0.0268(6)	0.033(3)
C(7)	0.6328(9)	0.8649(34)	0.1442(7)	0.035(3)
C(8)	0.6708(7)	0.9291(33)	0.0702(6)	0.025(3)
C(10)	0.6545(9)	1.2182(32)	-0.0448(7)	0.034(3)
C(11)	0.6190(9)	1.5003(31)	-0.1546(8)	0.049(4)
O(1)	0.6839(5)	0.6589(19)	0.1879(4)	0.029(5)
O(3)	0.7287(5)	1.1302(23)	-0.0730(4)	0.042(5)
O(2)	0.5628(6)	0.9748(24)	0.1673(4)	0.057(7)
O(4)	0.5950(5)	1.4214(23)	-0.0798(4)	0.042(5)
N	0.7535(6)	0.7809(22)	0.0517(5)	0.027(6)

Table 2 Fractional Atomic Coordinates and Thermal Parameters ($Å^2$) for the Hydrogen Atoms in 6-Bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one

Atom	x	y	z
Hn	0.7741	0.8994	0.0087
H(C2)	0.9012	0.4750	0.0305
H(C5)	0.7705	0.2569	0.2602
H(C6)	0.9215	0.0508	0.2266
H(C9)	0.5731	1.1862	0.0474
H1(C11)	0.6677	1.5778	-0.1560
H2(C11)	0.6126	1.3986	-0.1961
H3(C11)	0.5674	1.6441	-0.1715

Table 3 Bond Lengths (Å) for 6-Bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one

C(1) - Br	1.897(12)	O(1) - C(7)	1.369(15)
C(1) - C(2)	1.402(17)	C(7) - O(2)	1.169(16)
C(2) - C(3)	1.394(16)	C(7) - C(8)	1.483(17)
C(3) - C(4)	1.386(16)	C(8) - N	1.363(15)
C(4) - C(5)	1.370(17)	C(8) - C(9)	1.349(18)
C(5) - C(6)	1.371(17)	C(9) - C(10)	1.441(18)
C(6) - C(1)	1.367(17)	O(3) - C(10)	1.223(15)
C(3) - N	1.371(15)	O(4) - C(10)	1.345(16)
C(4) - O(1)	1.386(13)	O(4) - C(11)	1.445(16)

Table 4 Bond Angles (°) for 6-Bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one

C(2) - C(1) - Br	118.5(9)
C(6) - C(1) - Br	119.7(9)
C(2) - C(1) - C(6)	122.0(1)
C(1) - C(2) - C(3)	117.0(1)
C(2) - C(3) - C(4)	119.0(1)
C(2) - C(3) - N	121.0(1)
C(4) - C(3) - N	119.0(1)
C(3) - C(4) - C(5)	123.0(1)
C(3) - C(4) - O(1)	119.0(1)
C(5) - C(4) - O(1)	118.0(1)
C(4) - C(5) - C(6)	118.0(1)
C(5) - C(6) - C(1)	121.0(1)
C(3) - N - C(8)	124.0(1)
N - C(8) - C(7)	117.0(1)
N - C(8) - C(9)	125.0(1)
C(8) - C(7) - O(1)	117.0(1)
C(8) - C(7) - O(2)	125.0(1)
O(2) - C(7) - O(1)	118.0(1)
C(7) - O(1) - C(4)	123.5(9)
C(7) - C(8) - C(9)	117.0(1)
C(8) - C(9) - C(10)	121.0(1)
C(9) - C(10)- O(3)	127.0(1)
O(3) - C(10)- O(4)	121.0(1)
C(9) - C(10)- O(4)	112.0(1)
C(10)- O(4) - C(11)	115.9(9)

Table 5 Intermolecular Distances (Å) for 6-Bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one

Atom(1)	Atom(2)	distance	S	a	b	c
Br	...Br	4.23	-1	2.0	0.0	0.0
O(3)	...Br	3.13	-1	2.0	1.0	0.0
H(n)	...Br	3.14	-1	2.0	1.0	0.0
H(2)	...Br	3.17	-1	2.0	1.0	0.0
C(5)	...Br	3.70	2	2.0	0.0	0.0
C(6)	...Br	3.93	2	2.0	0.0	0.0
H(5)	...Br	3.27	2	2.0	0.0	0.0
C(11)	...O(1)	3.36	-2	0.0	3.0	0.0
O(4)	...O(2)	3.15	-1	1.0	2.0	0.0
C(11)	...O(2)	3.25	-1	1.0	2.0	0.0
H2(C11)	...O(2)	2.97	-1	1.0	3.0	0.0
H3(C11)	...O(2)	2.44	-1	1.0	2.0	0.0
C(11)	...O(2)	3.28	-2	0.0	3.0	0.0
H2(C11)	...O(2)	2.59	-2	0.0	3.0	0.0
H3(C11)	...O(2)	2.96	-2	0.0	3.0	0.0
H(9)	...O(4)	2.95	-1	1.0	3.0	0.0
C(9)	...C(3)	3.44	1	0.0	1.0	0.0
C(7)	...C(5)	3.47	1	0.0	1.0	0.0
C(11)	...H(5)	2.87	-2	0.0	2.0	1.0

Symmetry transformations: The second atom is related to the first atom, at (x, y, z) by the symmetry operation S with (a, b, c) added to the (x', Y', z') of S.
Where S = 1/2

Table 6 Intramolecular Distances (Å) for 6-Bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H--1,4-benzoxazin-2-one

C(2)	... Br	2.85	C(5)	... O(1)	2.37
H(2)	... Br	3.05	H(5)	... O(1)	2.46
O(2)	... O(1)	2.18	O(3)	... N	2.73
C(3)	... O(1)	2.39	C(8)	... O(3)	2.87
C(8)	... O(1)	2.43	Hn	... O(3)	1.87
O(4)	... O(3)	2.23	O(3)	... H1(C11)	2.57
C(9)	... O(3)	2.38	O(2)	... C(8)	2.36
O(3)	... H2(C11)	2.93	C(9)	... O(4)	2.32
C(9)	... O(2)	2.78	O(4)	... H1(C11)	1.86
H(9)	... O(2)	2.36	O(4)	... H3(C11)	1.94
H(9)	... O(4)	2.55	C(4)	... N	2.38
O(4)	... H2(C11)	2.13	C(7)	... N	2.43
C(2)	... N	2.41	H(2)	... N	2.47
C(9)	... N	2.41	C(4)	... C(1)	2.71
N	... C(10)	2.88	H(2)	... C(1)	2.08
C(3)	... C(1)	2.39	H(6)	... C(1)	1.97
C(5)	... C(1)	2.38	C(4)	... C(2)	2.40
H(5)	... C(1)	3.02	Hn	... C(3)	2.14
C(5)	... C(2)	2.81	C(6)	... C(3)	2.77
C(6)	... C(2)	2.42	C(8)	... C(3)	2.41
C(5)	... C(3)	2.42	H(2)	... C(3)	1.91
C(7)	... C(3)	2.81	C(6)	... C(4)	2.35
Hn	... C(2)	2.79	C(7)	... C(4)	2.43
Hn	... C(9)	2.38	H(5)	... C(4)	2.03
C(6)	... Br	2.83	H(6)	... C(5)	1.89
H(6)	... Br	2.97	C(7)	... C(9)	2.42
O(1)	... N	2.73	H(9)	... C(7)	2.36
C(8)	... Hn	1.85	C(11)	... C(10)	2.37

Table 6 cont.

H(9)	...C(10)	2.07	C(11)	...O(3)	2.62
H1(C11)	...C(10)	2.56	C(8)	...C(10)	2.43
C(8)	...C(4)	2.81	H(9)	...C(8)	1.78
H(6)	...C(1)	1.99	C(10)	...Hn	2.33
H(5)	...C(6)	2.20	C(10)	...H2(C11)	2.88

Table 7 Anisotropic Thermal coefficients ($Å^2$) for 6-Bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	0.042(1)	0.045(1)	0.014(1)	0.044(1)	0.012(1)	0.002(1)
N	0.033(5)	0.027(6)	0.011(6)	0.019(6)	0.006(5)	0.000(5)
O(1)	0.040(4)	0.027(5)	0.001(5)	0.020(6)	0.004(5)	0.009(4)
O(2)	0.054(5)	0.033(6)	0.001(6)	0.083(10)	0.028(6)	0.010(4)
O(3)	0.035(4)	0.042(5)	0.001(6)	0.047(6)	0.008(6)	0.004(4)
O(4)	0.046(5)	0.029(5)	0.004(6)	0.050(6)	0.027(6)	0.007(4)

Observed and Calculated Structure Factors for 6-Bromo-3,4-dihydro-3-(2-oxo-2-

ethoxy-ethylidene)-2H-1,4-benzoxazine-2-one (17, R = 6-Br)

H	K	L	10FO	10FC
3	0	0	1120	1100
4	0	0	573	-585
5	0	0	161	-150
6	0	0	1099	-1085
7	0	0	1034	-1009
8	0	0	769	-757
9	0	0	481	-515
10	0	0	376	-366
11	0	0	231	-131
15	0	0	177	222
16	0	0	234	296
1	1	0	103	-130
2	1	0	158	-164
3	1	0	129	68
4	1	0	501	-488
5	1	0	422	-407
6	1	0	203	-215
7	1	0	313	-313
8	1	0	175	158
11	1	0	221	252
12	1	0	266	331
0	2	0	388	403
2	2	0	381	383
4	2	0	196	-117
5	2	0	222	173
6	2	0	231	-228
8	2	0	185	-173
1	3	0	280	-278
2	3	0	441	-435
3	3	0	501	-526
4	3	0	605	-612
5	3	0	290	-357
6	3	0	411	-430
7	3	0	446	-469
8	3	0	201	179
10	3	0	246	168
11	3	0	300	303
13	3	0	254	265
0	4	0	279	-261
-12	1	1	226	-220
-11	1	1	211	-219
-10	1	1	621	-621
-9	1	1	514	-519
-8	1	1	466	-481
-5	1	1	182	83
-4	1	1	826	857
-3	1	1	384	397
-2	1	1	1444	1491
-1	1	1	776	762
0	1	1	718	725
1	1	1	608	-620
2	1	1	790	802
3	1	1	431	-447
4	1	1	869	-849
5	1	1	551	-534
6	1	1	675	-671
7	1	1	366	-373
8	1	1	213	-234
9	1	1	364	-333
10	1	1	312	314
14	1	1	349	-317
-12	2	1	354	334
-8	2	1	439	435
-7	2	1	676	635
-6	2	1	679	669
-5	2	1	493	511
-4	2	1	552	526
-3	2	1	347	-340
-1	2	1	474	-487
0	2	1	591	-582
1	2	1	790	-770
2	2	1	962	-994
3	2	1	399	-420
5	2	1	274	-264
7	2	1	194	178
8	2	1	427	437
9	2	1	363	343
11	2	1	520	525
12	2	1	196	255
-9	3	1	236	213
-8	3	1	258	-246
-6	3	1	253	219
-1	3	1	196	-187
0	3	1	329	-317
4	3	1	297	174
7	3	1	304	333
11	3	1	199	-168
-3	4	1	354	308
1	4	1	219	-275
3	4	1	302	-299
4	4	1	323	-360
5	4	1	217	-216
-3	5	1	266	-221
-14	0	2	281	-276
-13	0	2	348	-378
-12	0	2	402	-385
-11	0	2	382	-407
-10	0	2	707	-710
-9	0	2	346	-327
-8	0	2	664	633
-7	0	2	170	-137
-6	0	2	271	293
-5	0	2	747	730
-4	0	2	1006	956
-3	0	2	1408	1403
-2	0	2	225	231
2	0	2	324	-337
3	0	2	433	-473
4	0	2	948	-961
5	0	2	826	-815
6	0	2	876	-865
7	0	2	220	-230
8	0	2	310	-299
10	0	2	348	347
11	0	2	308	324
12	0	2	404	433
13	0	2	224	251
14	0	2	315	322
-9	1	2	293	295
-8	1	2	379	366
-7	1	2	427	442
-6	1	2	557	545
-5	1	2	573	547
-2	1	2	227	-232
-1	1	2	1171	-1166
0	1	2	136	-124
1	1	2	1178	-1132
2	1	2	1796	-1779
3	1	2	167	176
4	1	2	255	251
6	1	2	279	298
7	1	2	463	466
8	1	2	525	503
9	1	2	470	426
10	1	2	209	196
-12	2	2	304	-258
-6	2	2	417	416
-5	2	2	155	114
-4	2	2	271	279
-3	2	2	375	368
-2	2	2	322	301
-1	2	2	402	403
1	2	2	152	155
3	2	2	353	-374

H	K	L	10FO	10FC
-2	1	3	401	407
1	1	3	651	-643
2	1	3	2011	-1985
3	1	3	440	-451
4	1	3	747	-768
5	1	3	579	-591
8	1	3	328	350
9	1	3	275	256
10	1	3	509	507
11	1	3	255	211
13	1	3	346	355
-11	2	3	214	255
-10	2	3	392	420
-9	2	3	400	393
-8	2	3	462	487
-7	2	3	445	439
-5	2	3	420	-420
-3	2	3	386	-416
-2	2	3	740	-766
-1	2	3	653	-666
0	2	3	493	-508
1	2	3	511	-499
2	2	3	577	-556
3	2	3	568	529
6	2	3	658	683
7	2	3	463	478
8	2	3	593	586
9	2	3	464	502
13	2	3	328	-285
14	2	3	212	-202
-1	3	3	205	157
7	3	3	194	-209
-1	4	3	232	-204
0	4	3	300	-310
1	4	3	263	-171
7	4	3	233	211
-12	0	4	243	-254
-11	0	4	315	-321
-10	0	4	234	-256
-9	0	4	205	223
-8	0	4	282	265
-7	0	4	812	821
-5	0	4	891	913
-4	0	4	797	787
-3	0	4	804	782
-2	0	4	550	544
-1	0	4	927	-896
0	0	4	151	-153
1	0	4	1630	-1700
2	0	4	1494	-1534
3	0	4	912	-913
4	0	4	1063	-1037
5	0	4	406	-397
6	0	4	385	-390
7	0	4	607	613
8	0	4	386	389
9	0	4	560	551
12	0	4	819	781
15	0	4	518	484
-12	1	4	470	459
-8	1	4	228	216
-7	1	4	251	259
-6	1	4	274	257
-5	1	4	337	347
-3	1	4	470	-480
-2	1	4	715	-689
-1	1	4	667	-633
0	1	4	473	-489
1	1	4	292	303
2	1	4	415	370
3	1	4	275	-256
4	1	4	287	292
-4	1	4	417	431
-3	1	4	148	179
-2	1	4	288	290
-1	1	4	275	279
0	1	4	219	-225
1	1	4	323	-304
3	1	4	283	271
5	1	4	266	284
6	1	4	455	431
7	1	4	581	-573
8	1	4	229	224
9	1	4	609	-607
10	1	4	165	217
12	1	4	221	186
14	1	4	375	400
-12	2	4	211	-194
-11	2	4	218	-277
-7	2	4	403	-437
-6	2	4	471	-479
-5	2	4	574	-537
-4	2	4	634	-573
-3	2	4	335	-318
-2	2	4	340	354
0	2	4	426	429
1	2	4	550	569
3	2	4	591	601
4	2	4	426	460
6	2	4	215	-213
11	2	4	262	275
12	2	4	226	-175
-3	3	4	286	303
3	3	4	310	327
5	3	4	487	495
8	3	4	549	551
-5	4	4	395	435
3	4	4	363	342
-4	1	5	275	236
-3	1	5	338	314
-2	1	5	259	285
-1	1	5	700	703
0	1	5	421	414
1	1	5	162	158
3	1	5	251	-259
5	1	5	797	-802
6	1	5	677	-700
7	1	5	740	-772
8	1	5	1559	-1583
9	1	5	656	-671
10	1	5	279	-294
12	1	5	437	444
14	1	5	549	515
-12	2	5	577	536
-11	2	5	855	838
-7	2	5	614	631
-6	2	5	374	372
-5	2	5	353	325
-4	2	5	184	191
-3	2	5	417	-407
-2	2	5	413	-441
0	2	5	227	244
1	2	5	214	-216
3	2	5	335	-335
4	2	5	544	-549
6	2	5	580	-552
11	2	5	221	209
12	2	5	345	-373
-3	3	5	422	443
3	3	5	600	635
5	3	5	215	204
8	3	5	537	526
-5	4	5	776	759
3	4	5	496	500

H	K	L	10FO	10FC
5	1	6	157	-155
7	1	6	192	-195
8	1	6	378	-385
9	1	6	263	-216
10	1	6	463	-436
11	1	6	297	-335
-11	2	6	191	183
-9	2	6	183	109
-8	2	6	196	163
-6	2	6	230	-225
-4	2	6	177	-138
-3	2	6	537	-519
-1	2	6	335	-339
0	2	6	187	-207
1	2	6	376	-361
2	2	6	210	-207
4	2	6	473	460
5	2	6	299	305
6	2	6	227	202
7	2	6	304	319
8	2	6	213	221
9	2	6	177	185
-7	3	6	373	-401
-6	3	6	446	-440
-5	3	6	331	-317
-4	3	6	325	-303
-1	3	6	272	306
0	3	6	220	229
1	3	6	354	365
2	3	6	559	541
3	3	6	317	319
4	3	6	320	305
8	3	6	298	-321
9	3	6	268	-264
11	3	6	233	-247
3	4	6	261	-265

H	K	L	10FO	10FC
-13	1	7	199	246
-11	1	7	243	287
-10	1	7	464	471
-9	1	7	225	177
-6	1	7	456	-467
-5	1	7	401	-390
-4	1	7	708	-693
-3	1	7	1113	-1087
-2	1	7	221	-247
-1	1	7	445	-462
1	1	7	261	252
2	1	7	710	658
3	1	7	665	661
4	1	7	183	190
5	1	7	754	768
6	1	7	370	402
7	1	7	242	271
9	1	7	167	-126
10	1	7	213	-195
11	1	7	213	-190
12	1	7	201	-183
13	1	7	282	-296
14	1	7	208	-188
-10	2	7	371	-392
-9	2	7	249	-259
-8	2	7	465	-458
-7	2	7	410	-419
-6	2	7	475	-453
-4	2	7	230	257
-2	2	7	447	472
-1	2	7	575	617
0	2	7	544	564
1	2	7	598	550
2	2	7	454	472
3	2	7	161	159
6	2	7	284	-309

H	K	L	10FO	10FC
7	2	7	396	-424
8	2	7	447	-437
9	2	7	343	-383
-2	3	7	190	201
2	3	7	232	-215
6	3	7	269	-232
7	3	7	260	257
0	4	7	275	275
1	4	7	348	286
-14	0	8	290	285
-13	0	8	396	412
-12	0	8	282	220
-11	0	8	330	337
-9	0	8	537	-541
-8	0	8	493	-538
-7	0	8	503	-470
-6	0	8	541	-533
-5	0	8	891	-879
-4	0	8	465	-483
-2	0	8	769	755
-1	0	8	493	458
0	0	8	373	-348
1	0	8	1092	1143
2	0	8	776	792
3	0	8	618	637
4	0	8	462	456
5	0	8	1070	1005
6	0	8	224	242
7	0	8	618	-564
8	0	8	498	-483
9	0	8	409	-427
11	0	8	409	-386
12	0	8	542	-548
-10	1	8	352	-400
-7	1	8	371	-424
-6	1	8	152	24

H	K	L	10FO	10FC
-5	1	9	309	-267
-4	1	9	262	-266
-3	1	9	227	246
-2	1	9	281	263
-1	1	9	316	359
0	1	9	478	464
1	1	9	948	930
2	1	9	588	566
3	1	9	383	347
4	1	9	182	201
6	1	9	256	-269
7	1	9	464	-448
8	1	9	241	-239
9	1	9	323	-310
10	1	9	333	-339
-11	2	9	294	-342
-6	2	9	273	253
-5	2	9	490	444
-4	2	9	437	446
-3	2	9	469	478
-2	2	9	503	498
-1	2	9	270	276
0	2	9	211	223
1	2	9	222	-202
2	2	9	305	-279
3	2	9	332	-321
4	2	9	626	-620
5	2	9	374	-390
6	2	9	290	-302
7	2	9	278	-274
9	2	9	196	175
3	3	9	425	-405
4	4	9	328	363
3	4	9	243	-136
-12	0	10	264	-135
-11	0	10	338	-334

H	K	L	10FO	10FC
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-9	0	10	501	-463
-8	0	10	1006	-1002
-6	0	10	350	-353
-5	0	10	171	-138
-4	0	10	342	330
-2	0	10	740	750
-1	0	10	948	979
0	0	10	495	505
1	0	10	797	787
2	0	10	225	243
4	0	10	359	-373
5	0	10	509	-495
6	0	10	203	-190
7	0	10	605	-557
8	0	10	356	-332
9	0	10	256	-256
-7	1	10	372	398
-6	1	10	332	333
-5	1	10	243	206
0	1	10	599	-607
1	1	10	196	-213
3	1	10	449	-422
4	1	10	414	-407
7	1	10	164	-160
8	1	10	209	226
9	1	10	313	343
-8	2	10	185	-166
-2	2	10	191	226
-1	2	10	353	365
0	2	10	215	233
7	2	10	227	-227
10	2	10	228	-239
-6	3	10	232	277
-5	3	10	349	352
-4	3	10	320	282
-2	3	10	348	345
0	3	10	269	-288
1	3	10	204	-146
2	3	10	346	-380
3	3	10	387	-338
4	3	10	254	-277
5	3	10	377	-368
6	3	10	233	-138
0	4	10	254	-255
-12	1	11	226	-204
-11	1	11	241	-248
-10	1	11	236	-306
-9	1	11	374	-374
-8	1	11	182	-174
-7	1	11	218	221
-4	1	11	401	388
-3	1	11	647	622
-2	1	11	325	337
-1	1	11	524	516
2	1	11	208	228
3	1	11	519	-498
4	1	11	215	-212
5	1	11	413	-387
6	1	11	412	-438
7	1	11	388	-371
8	1	11	221	-261
-9	2	11	196	205
-8	2	11	264	283
-7	2	11	297	287
-6	2	11	325	314
-5	2	11	438	448
-4	2	11	203	154
-1	2	11	413	-442
0	2	11	682	-692
1	2	11	211	-250
2	2	11	268	-273
3	2	11	213	-187
-6	1	14	280	-330
-5	1	14	271	-229
-4	1	14	269	-238
-3	1	14	320	329
1	1	14	459	467
2	1	14	197	171
4	1	14	291	306
5	1	14	221	-208
9	1	14	218	204
-6	2	14	255	-294
-1	2	14	324	-321
-2	3	14	256	-237
-1	3	14	222	196
3	3	14	309	346
5	3	14	208	192
-10	1	15	215	227
-9	1	15	315	-358
-3	1	15	249	-297
-2	1	15	282	-331
-1	1	15	478	-476
2	1	15	247	249
4	1	15	335	389
6	1	15	210	150
7	1	15	223	235
8	1	15	235	-224
-7	2	15	369	-438
-5	2	15	227	-266
-4	2	15	291	289
0	2	15	219	253
1	2	15	232	275
2	2	15	223	252
4	2	15	234	-184
-6	0	16	286	-296
-5	0	16	489	-502
-4	0	16	389	-382
-3	0	16	612	-585
-2	0	16	196	172
-1	0	16	340	350
0	0	16	196	218
1	0	16	240	-236
2	0	16	266	-265
3	0	16	416	-425
4	0	16	493	485
5	0	16	309	282
6	0	16	686	649
7	0	16	519	528
8	0	16	419	423
9	0	16	608	-607
-5	1	16	442	462
-4	1	16	290	-277
-2	1	16	426	-413
0	1	16	557	-603
1	1	16	608	-607
2	1	16	515	-503
4	1	16	367	-360
5	1	16	462	-438
-10	2	16	340	305
-8	2	16	282	312
-7	2	16	396	371
-6	2	16	366	364
-5	2	16	176	-201
-2	2	16	385	-386
-1	2	16	230	-199
0	2	16	246	-222
1	2	16	241	274
2	2	16	216	263
4	2	16	443	476
6	2	16	324	-350
7	2	16	279	-241
8	2	16	322	299
11	2	16	397	-424
-7	3	16	320	-316

H	K	L	10FO	10FC
-2	0	16	457	-437
3	0	16	579	576
4	0	16	664	645
6	0	16	263	255
7	0	16	279	277
-9	1	16	255	-184
6	1	19	202	-210
-4	0	20	233	307
-3	0	20	229	216
-2	0	20	234	210
0	1	20	206	-141
2	1	16	277	261
-6	1	17	330	-380
2	1	17	237	268
3	1	17	236	176
0	2	17	210	208
5	2	17	227	-206
-7	0	18	289	-304
-3	0	18	248	-260
-1	0	18	250	184
0	0	18	233	195
1	0	18	274	299
4	0	18	467	454
8	0	18	271	-258
5	1	18	253	-288
-7	1	19	212	-174

TITLE STUDIES OF COMPLEXES DERIVED FROM 5-ACETYLAMINO-1,2-BENZOQUINONE 2-OXIME AND RELATED LIGANDS

AUTHOR HENGAMEH BARJESTEH

INSTITUTION and DATE (North London Polytechnic) CNAA. 1991

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